CCXLVI.—*Optical Activity and the Polarity of Substituent Groups. Part XV. Phenyl-substituted Esters and Ethers of* l-*Menthol and β-Octyl Alcohol.*

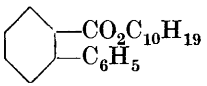
By H. GORDON RULE and JAMES BAIN.

THE change in the optical activity of an organic compound due to the accumulation of phenyl radicals on an atom near an asymmetric group has been discussed by Hilditch (*Z. physikal. Chem.*, 1911, **77**, 482), who suggested that this type of substitution leads to a degree of molecular symmetry which frequently results in diminished rotatory power. A remarkable example of this nature was subsequently discovered by Tschugaev (*Ber.*, 1912, **35**, 2759) in the case of *l*-menthyl triphenylacetate, the rotation of which is lowered to such an extent that in certain solvents the sign becomes reversed. Now, in earlier communications of this series it has been established that the rotatory powers of menthyl and β-octyl esters of substituted acetic acids vary with the polarity of the substituent, in such a manner that the more electronegative the latter, the greater is the dissociation constant of the acid and the higher is the rotatory power of the ester (see preceding paper). It appeared possible, therefore, that the low rotation of the triphenylacetate might be a consequence of the parent acid possessing a low dissociation constant. This idea seemed to be confirmed, not only by the observations of Elbs and Tölle (*J. pr. Chem.*, 1885, **32**, 624) and of Schmidlin and Hodgson (*Ber.*, 1908, **41**, 441), who describe the compound as an extremely weak acid, but also from a consideration of the known properties of triphenylmethyl halides, in which the aryl radical functions as a positive ion. It was therefore at first supposed that triphenylmethyl—unlike the mono- and di-phenylmethyl radicals—exerted an electron repulsion in the sense

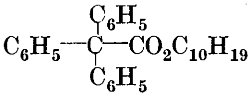
$$\underset{\longrightarrow}{(C_6H_5)_3\overset{+}{C}\text{——}\overset{-}{Cl}} \qquad \underset{\longrightarrow}{(C_6H_5)_3C\cdot CO\overset{-}{O}\text{——}\overset{+}{H}}$$

Shift assisting ionisation. Shift repressing ionisation.

A study of the literature relating to optically active phenyl-substituted compounds, however, reveals a second possibility. It has been shown (Bretscher, Rule, and Spence, J., 1928, 1493) that the rotatory power of *l*-menthyl benzoate, $[M]_{5461}$ $-281°$ (in benzene, $c = 5$) is depressed by the introduction of a phenyl group into the ortho-position, *l*-menthyl diphenyl-2-carboxylate having $[M]_{5461}$ $-233°$ (in benzene, $c = 5$). This low rotation was assumed to result from the spatial proximity of the phenyl group to the active complex. A similar reason may be advanced for the abnormally low rotatory power observed by Rupe and Münter (*Annalen*, 1909, **369**, 339) for *l*-menthyl δ-phenylvalerate, for which $[M]_D$ is $-107°$ as compared with the average value for an aliphatic ester of approximately $-157°$. The researches of Frankland and of Pickard and Kenyon on the influence of growing chains suggest that in the δ-phenylvalerate the natural curvature of the carbon chain will bring the phenyl group into the neighbourhood of the menthyl radical. Possibly, therefore, the optical properties of *l*-menthyl triphenylacetate are due to the accumulation of bulky phenyl groups on the same carbon atom resulting in the benzene nuclei being forced into positions relatively close to the active complex.



$C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2C_{10}H_{19}$



$$C_6H_5\text{—}\overset{C_6H_5}{\underset{C_6H_5}{C}}\text{—}CO_2C_{10}H_{19}$$

It is of interest to note that the initial rise in the rotatory powers of *l*-menthyl mono- and di-phenylacetates, followed by a fall in the tri-substituted compound, has also its parallel in the aliphatic series, not only in respect of rotatory power but also of the degree of electrolytic dissociation. This may be illustrated, for example, by the following data referring to the mono-, di-, and tri-methyl-substituted acetic acids and their menthyl esters.

Acid.	Value of $K \times 10^5$.	$[M]_D$ of ester (Rupe).
$CH_3{\cdot}CH_2{\cdot}CO_2H$	1·4	−160·2°
$(CH_3)_2CH{\cdot}CO_2H$	1·5	−163·5
$(CH_3)_3C{\cdot}CO_2H$	0·98	−161·5

A further example is to be found in the isomeric butyl esters of *d*-mandelic acid recently investigated by Wood, Chrisman, and Nicholas (J., 1928, 2180), among which the tertiary compound exhibits the lowest rotatory power.

	$[\alpha]^{15°}_{5461}$.
$C_6H_5{\cdot}CH(OH){\cdot}CO_2CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	−110·0°
$C_6H_5{\cdot}CH(OH){\cdot}CO_2CH_2{\cdot}CH(CH_3)_2$	−123·5
$C_6H_5{\cdot}CH(OH){\cdot}CO_2C(CH_3)_3$	− 94·5

Here, again, the alternating influence of the *n*-, *iso*-, and *tert*.-butyl groups on the optical activity is repeated in the dissociation constants of the corresponding butyric acids, for which the following values of $K \times 10^5$ are recorded : Valeric acid, 1·6; *iso*valeric acid, 1·73; trimethylacetic acid, 0·98.

In order to ascertain whether the depressive influence of the triphenylmethyl group on the rotatory power is a general property, the *l*-menthyl and β-*octyl* ethers of mono-, di-, and tri-phenyl-carbinols, and the β-*octyl* esters of mono-, di-, and tri-phenylacetic acids have been prepared and examined. d-*Bornyl triphenylmethyl ether* was also prepared in order to determine the sign of the rotation, but on account of their known tendency to isomerise, the bornyl derivatives were not further investigated.

Since the only available evidence bearing on the acidic strength of triphenylacetic acid is of a qualitative nature, it was thought advisable to make a direct comparison of the conductivities of mono-, di-, and tri-phenylacetic acids in equivalent solutions (see below).

Values of $[M]^{20°}_D$ *for phenyl-substituted esters of* l-*menthol and of* β-*octyl alcohol.* (In solvents, c = 5.)

	R = *l*-Menthyl.		R = *l*-β-Octyl.	
$CH_3{\cdot}CO_2R$	−157·4°	(homog.)	−11·8° [3]	(homog.)
$C_6H_5{\cdot}CH_2{\cdot}CO_2R$	−185	(homog.) [1]	−43·4	(homog.)
			−25	(C_6H_6)
			−61	(EtOH)
$(C_6H_5)_2CH{\cdot}CO_2R$	−277 [1]		−70·5	(homog.)
			−40	(C_6H_6)
			−99	(EtOH)
$(C_6H_5)_3C{\cdot}CO_2R$	+58·7	(CS_2) [2]	+34	(CS_2)
	−14·6	(toluene) [2]	+ 0·6	(C_6H_6)
			−33	(EtOH)

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[1] Rupe, *Trans. Faraday Soc.*, 1914, **10**, 47.

[2] Tschugaev and Glinin, *Ber.*, 1912, **45**, 2760 (c = 17—19).

[3] Pickard and Kenyon, J., 1914, **105**, 835.

Values of $[\mathrm{M}]_{\mathrm{D}}^{20^\circ}$ *for phenyl-substituted ethers of menthol and of β-octyl alcohol.*

	R = *l*-Menthyl.	R = *l*-*β*-Octyl.
$CH_3 \cdot O \cdot R$	−162·9° (homog.)[1]	—
$C_6H_5 \cdot CH_2 \cdot O \cdot R$	−233 (homog.)[1]	− 60·1° (homog.) − 59 (C_6H_6) − 54 (EtOH)
$(C_6H_5)_2CH \cdot O \cdot R$	— −627 (C_6H_6) −545 (acetone)	−117·7 (homog.) −103 (C_6H_6) − 91 (EtOH)
$(C_6H_5)_3C \cdot O \cdot R$	— −473 (C_6H_6) −454 (acetone)	+ 59·6 (homog.) + 47 (C_6H_6) + 72 (EtOH)

[1] Tschugaev, *Chem. Z.*, 1902, 1238.

In each of the above series the introduction of the first and second phenyl groups into the molecule leads to successively increasing rotatory powers. The union of the third phenyl residue to the same carbon atom, on the other hand, results in a fall, which, except in the case of the *l*-menthyl ether, is so pronounced as to cause an inversion in sign. It was anticipated that the shorter distance between the triphenylmethyl group and the asymmetric complex in the ethers as compared with the esters would result in a greater tendency to inversion on the part of the former compounds. This expectation is realised in the *l*-octyl series, in which the dextrorotation is of a high order of magnitude. In the *l*-menthyl di- and tri-phenylmethyl ethers it is possible that the high lævorotation arises from the secondary effect of the benzene nuclei on the other asymmetric atoms of the menthyl radical. Evidence for the *d*-bornyl ethers is incomplete, but the relatively high rotatory power of the trisubstituted ether, $[M]_{\mathrm{D}}^{20^\circ}$ + 190° (in benzene, $c = 5$) indicates that the triphenylmethyl radical produces no abnormal lowering of rotation. Similarly, the triphenylacetic ester of *l*-borneol, for which Tschugaev and Glinin (*loc. cit.*) record $[M]_{\mathrm{D}}^{20^\circ}$ − 81·2° (in toluene, $c = 17$), has been observed by these authors to have a rotation not markedly different from the corresponding average aliphatic ester ($[M]_{\mathrm{D}} = -$ 88°).

Molecular Conductivities of the Acids.—No attempt was made to determine the dissociation constants of the acids, since the trisubstituted compound is practically insoluble in water at ordinary temperatures. Consequently, as has been observed by Elbs and Tölle and by Schmidlin and Hodgson (*locc. cit.*), an aqueous solution of the sodium salt of triphenylacetic acid is only stable in high concentrations. On dilution, the free acid is progressively liberated by hydrolytic dissociation and precipitated. A comparison was therefore made of the molar conductivities of the acids at similar dilutions in aqueous alcohol.*

Molar conductivities of phenyl-substituted acetic acids in aqueous alcohol (60 vols. EtOH, 40 vols. H_2O) at 20°.

Dilution.	Phenylacetic.	Diphenylacetic.	Triphenylacetic.
64	0·78	0·79	—
128	1·11	1·13	—
256	1·55	1·61	—
512	2·14	2·30	2·53
1024	3·11	3·30	3·50

The above figures show definitely that the trisubstituted acid does not possess the properties of an extremely weak acid, and that the parallel previously established between the dissociation constants of the acids and the rotatory powers of the esters cannot be upheld in the case of the triphenyl derivatives. Taking into consideration the size and probable high viscosity of the triphenylacetic anion, we do not doubt that this acid is in reality the strongest of the series. The alternative suggestion may therefore be adopted, *viz.*, that the lowered rotatory powers of the triphenyl-substituted esters and ethers are a consequence of the accumulation of phenyl radicals on one carbon atom, which has the effect of forcing these groups into close spatial proximity to the active complex. Similar depressions, as already stated, are observed in the analogous cases of *l*-menthyl diphenyl-2-carboxylate and *l*-menthyl δ-phenylvalerate.

Dispersion.—When the reciprocal of the rotation is plotted against the square of the wave-length of the light employed, it is found that the deviations from the linear are in most cases small. Larger divergences are observed for the *d*-bornyl ether in acetone and in ethyl acetate. *l*-Octyl triphenylacetate has definitely anomalous dispersion in benzene solution, thus resembling the corresponding *l*-menthyl ester investigated by Rupe. This abnormality is not unexpected, as in both these cases the rotation is not far removed from zero.

EXPERIMENTAL.

The *l*-menthol employed in the following preparations had $[\alpha]_D^{20°}$ − 49·75° (in alcohol, $c = 10$) : the β-octanol was obtained by the method of Pickard and Kenyon and gave $[\alpha]_{5461}^{20°} \pm 9·6°$ in the homogeneous state.

l-Menthyl triphenylmethyl ether was prepared from triphenylmethyl chloride, *l*-menthol, and pyridine, according to the directions given by Schmidlin (*Ber.*, 1912, **45**, 3188), who did not

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* The authors wish to thank Messrs. A. Robertson and J. Robertson for preliminary conductivity determinations with these acids, and for confirming the results qualitatively by colorimetric tests with " Universal " indicator.

examine the rotatory power of the ether. The pale yellow crystalline compound was recrystallised from hot alcohol until the rotatory power was constant; m. p. 136° (Schmidlin, m. p. 135—136°).

Triphenylmethyl l-β-*octyl ether* was obtained in a similar manner to the above, from *l*-β-octyl alcohol (10 g.), triphenylmethyl chloride (9 g.), and pyridine (23 g.). The mixture was heated for 5 hours, washed free from pyridine and hydrogen chloride, and dried. After removal of the excess of octyl alcohol under diminished pressure, a yellow product remained which deposited fine crystals on standing. The latter proved to be triphenylcarbinol, m. p. 159°, derived probably from the aqueous hydrolysis of the ether during the washing process. The liquid portion was distilled and the fraction boiling at 178°/0·3 mm. was collected separately; yield, 6 g. If allowed to stand in contact with moist air, hydrolysis occurs with deposition of triphenylcarbinol. Similarly, when a sample was warmed with methyl alcohol and animal charcoal the compound was converted into the methyl ether (Found: C, 87·0; H, 8·6. $C_{27}H_{32}O$ requires C, 87·1; H, 8·7%).

d-*Bornyl triphenylmethyl ether* was prepared in the same manner from *d*-borneol having $[\alpha]_D^{17^\circ} = +30·5^\circ$ (in alcohol, $c = 5$). The white crystalline ether was recrystallised from methyl alcohol until pure; it then melted at 116°; yield, 10 g. of purified product from 20 g. of *d*-borneol (Found: C, 87·65; H, 8·3. $C_{29}H_{32}O$ requires C, 87·8; H, 8·15%).

l-*Menthyl diphenylmethyl ether.* Pure dry benzhydrol (14 g.) was dissolved in dry benzene (100 c.c.) and some fused calcium chloride added to the mixture. Dry hydrogen chloride was passed into the boiling solution for about 2 hours, after which the benzene layer was separated, the solvent distilled off on the oil-bath and the remaining liquid distilled in a vacuum. Diphenylmethyl chloride was collected between 155° and 157°/12 mm.; yield 14 g.

The diphenylmethyl chloride (14 g.) in toluene was added to a toluene solution of *l*-menthol (20 g.) in which sodium (1·2 g.) had been dissolved. The mixture was boiled gently for 8 hours, during which a slow evolution of hydrogen chloride took place, due probably to the interaction between menthol and diphenylmethyl chloride. After cooling, the mixture was diluted with ether, washed with water, and dried over calcium chloride. The excess of solvents and menthol were distilled off under reduced pressure, and the yellow solid which remained was recrystallised from methyl alcohol. l-*Menthyl diphenylmethyl ether* crystallised in fine white needles, m. p. 67°; yield of pure ether, 15 g. (Found: C, 85·5; H, 9·3. $C_{23}H_{30}O$ requires C, 85·6; H, 9·4%).

Diphenylmethyl l-β-*octyl ether*. This was first prepared in a similar manner to the menthyl ether, from potassium octyloxide (from a toluene solution of 10 g. of octyl alcohol in which 2 g. of potassium had been dissolved) and diphenylmethyl chloride (15 g.). Much difficulty was encountered in obtaining good yields of this ether : on removal of the excess of toluene and octyl alcohol under diminished pressure, a crystalline solid, m. p. 215—220°, was deposited on the sides of the flask; the substance might be tetraphenylethylene, m. p. 221°, since diphenylmethyl chloride is known to decompose at high temperatures to give this compound together with hydrogen chloride. Better yields of the *ether* were obtained by using smaller proportions of diphenylmethyl chloride. From 7 g. of the latter, 15 g. of *l*-β-octyl alcohol, and 1·7 g. of potassium in toluene solution, 3 g. of an octyl ether, b. p. 202°/10 mm., were isolated, the rotatory power of which was unchanged on further fractionation (Found : C, 84·8; H, 9·6. $C_{21}H_{28}O$ requires C, 85·1; H, 9·5%).

Benzyl l-β-*octyl ether*. A toluene solution of 11 g. of *l*-octyl alcohol, in which 2 g. of potassium had been dissolved, was treated with 15 g. of freshly distilled benzyl chloride and gently boiled for two hours. From the reaction mixture was isolated *benzyl octyl ether*, b. p. 154°/18 mm., which was fractionated until of constant rotation; yield of pure ether, 10 g. (Found : C, 81·7; H, 10·8. $C_{15}H_{24}O$ requires C, 81·7; H, 11·0%).

l-β-*Octyl phenylacetate* was prepared from phenylacetic acid, m. p. 74·5°. This was treated with thionyl chloride and the resulting phenylacetyl chloride fractionated, giving a colourless liquid, b. p. 94°/10 mm. The latter was converted into the octyl ester, pyridine being used as catalyst. The ester was obtained as a somewhat yellowish liquid, b. p. 174°/12 mm., which still retained its colour on further fractionation (Found : C, 77·1; H, 9·8. $C_{16}H_{24}O_2$ requires C, 77·35 ; H, 9·75%).

d-β-*Octyl diphenylacetate*. Benzilic acid was converted into diphenylacetic acid by reduction with hydriodic acid and red phosphorus in glacial acetic acid solution. The recrystallised diphenylacetic acid melted at 146° (Symons and Zincke, *Annalen*, 1874, **171**, 126, quote m. p. 145—146°). This product contained no benzilic acid as it gave no violet coloration with concentrated sulphuric acid.

The well-dried diphenylacetic acid (16 g.) and thionyl chloride (24 g.) were heated together on an oil-bath for 2 hours. After removing the excess of thionyl chloride under diminished pressure, the crystalline residual mass was dissolved in pyridine (20 g.) and *d*-β-octyl alcohol added. The reaction was completed by heating for 4 hours at 120°. d-β-*Octyl diphenylacetate* was isolated from this mixture as a colourless liquid, b. p. 221°/17 mm.; yield of pure ester, 20 g. (Found : C, 81·4; H, 8·8. $C_{22}H_{28}O_2$ requires C, 81·4; H, 8·7%).

d-β-*Octyl triphenylacetate.* The experimental details given by Schmidlin and Hodgson (*Ber.*, 1906, **39**, 634) for the preparation of triphenylacetic acid gave only extremely small yields. The best results were obtained by mixing well-dried triphenylmethyl chloride (33 g.) with magnesium turnings (5 g.) which had previously been thoroughly washed with ether, and dried for 3—4 hours at 100°. The mixture was placed in a 500-c.c. flask, fitted with a cork bearing a mercury seal and stirrer, a reflux condenser, a small glass tube for the addition of ether, and a wide glass tube through which carbon dioxide was passed into the flask. When all the air had been displaced, 300 c.c. of dry ether were added without interrupting the passage of the gas. The mixture was well stirred, and the flask warmed gently on the water-bath. Further treatment was according to the method of Schmidlin and Hodgson; yield of triphenylacetic acid 27 g., m. p. 263°. Since these details were evolved similar conditions have been published by Gilman and Zoellner (*J. Amer. Chem. Soc.*, 1929, **51**, 3493).

Pure triphenylacetic acid (20 g.) was converted into the pure acid chloride, m. p. 126—127°, and thence by treatment with potassium octyloxide into d-*octyl triphenylacetate.* The ester was obtained as a pale yellow viscous liquid, b. p. 206°/0·03 mm.; yield 14 g. The rotatory power in benzene was unchanged on further fractionation (Found : C, 83·8; H, 8·0. $C_{28}H_{32}O_2$ requires C, 83·9; H, 8·05%).

Determinations of Rotatory Power and Density.—Measurements of rotatory power in solution recorded in the following tables all refer to a concentration of approximately $c = 5$.

l-β-*Octyl phenylacetate* ($d_{4°}^{20°}$ 0·9578).

Solvent.	l.	t.	$[M]_{6708}^{20°}$.	$[M]_{5893}^{20°}$.	$[M]_{5461}^{20°}$.	$[M]_{4358}^{20°}$.
Homog.	50	20°	−33·9°	−43·4°	−52·3°	—
Benzene	100	20	−20	−25	−31	− 70°
EtOH	100	20	−42	−61	−72	−113

d-β-*Octyl diphenylacetate* ($d_{4°}^{15°}$ 0·9974).

Homog.	100	15	+53·0	+70·5	+ 84·7	+147·8
Benzene	100	20	+29	+39·5	+ 48	+ 85
EtOH	100	14	+78	+99	+119	+220

d-β-*Octyl triphenylacetate.*

Alcohol	200	20	+28	+33	+41	+64
$CHCl_3$	200	20	+23	+29	+35	+56
Acetone	200	20	+21	+28	+35	+56
Benzene	200	20	+ 1·3	− 0·6	− 2	− 6
CS_2	200	20	−24	−34	−44	−94

Benzyl l-β-*octyl ether* ($d_{4^{\circ}}^{20^{\circ}}$ 0·8974).

Homog.	50	20	−45·8	−60·1	−71·3	−120·4
Benzene	200	20	−46	−59	−68	−116
EtOH	200	20	−42	−54	−64	−109

Diphenylmethyl l-β-*octyl ether* ($d_{4^{\circ}}^{17^{\circ}}$ 0·9675).

Homog.	25	17	−88·7	−117·7	−138·9	−246·2
Benzene	100	17	−83	−103	−123	−228
EtOH	100	17	−72	− 91	−108	−193

l-*Menthyl diphenylmethyl ether.*

Benzene	200	17	−474	−627	−748	−1299
Ethyl acetate	200	17	−421	−562	−668	−1157
Acetone	200	17	−412	−545	−650	−1117

l-*Menthyl triphenylmethyl ether.*

Benzene	100	11	−365	−473	−550	−968
Acetone	100	18·5	−348	−454	−532	−881
Ethyl acetate	100	18·5	−335	−434	−518	−826

Triphenylmethyl l-β-*octyl ether* ($d_{4^{\circ}}^{16^{\circ}}$ 1·026).

(Homog.) ...	25	16	—	+59·6	+71·1	—
Alcohol	100	16	+54	+72	+92	+175
Benzene	100	16	—	+47	+57	+104

d-*Bornyl triphenylmethyl ether.*

Benzene	100	19	+138	+190	+225	+385
Ethyl acetate	100	19	+ 94	+165	+193	+337
Acetone	100	19	+109	+159	+191	+317

Summary.

A comparison of *l*-menthyl and β-octyl esters of mono-, di-, and tri-phenylacetic acids and of the corresponding mono-, di-, and tri-phenylmethyl ethers shows that the rotatory powers rise successively with the introduction of the first and second phenyl groups into the molecule, but fall on the insertion of a third. Except in the case of the *l*-menthyl ether, the presence of the triphenylmethyl complex leads to an inversion of sign.

These optical effects in the esters do not correspond to the alteration in acidic strength of the acids, for triphenylacetic acid is now shown to be the most highly dissociated acid of the series. The statements in the literature describing it as an extremely weak acid are therefore incorrect.

Whatever may be the reason for the depressive effect of the triphenylmethyl radical on the rotation, it is suggested that it is related to the enforced spatial proximity of the phenyl groups to the active complex. Similar depressions are caused by the phenyl group when introduced into the ortho-position in *l*-menthyl benzoate, and into the δ-position in *l*-menthyl valerate. In the δ-phenylvalerate the normal bending of the methylene chain may be supposed to bring the terminal cyclic groups into closer proximity than in the α- or β-substituted compounds, in which a rise of rotation occurs.

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