

LII.—*Optical Activity of Certain Ethers and Esters.*

By Professor PHILIPPE A. GUYE.

In a recent publication, Messrs. John McCrae and T. S. Patterson (Trans., 1900, '77, 1096) have directed attention to the very interesting properties of the acetyl and phenacetyl derivatives of diethyl *d*-tartrate, and have shown that, according to their own observations and others made in Professor Frankland's laboratory, the phenacetyl group, which has a mass approximately equal to that of the toluyl group, nevertheless influences the rotatory power in a way which connects the phenacetyl group more closely with the acetyl group, or even the chloracetyl group, than with the toluyl group. In support of this conclusion, Messrs. McCrae and Patterson only quote Tschugaeff's previous observations (*Ber.*, 1898, 31, 360, 1778). As various researches prosecuted in my laboratory confirm Messrs. McCrae and Patterson's conclusions (Guye and Chavanne, *Bull. Soc. Chim.*, 1896, [iii], 15, 177; *Arch. Sci. phys. nat. Genève*, 1896, [iii], 1, 34, 121; Welt, *Ann. Chim. Phys.*, 1895, [vii], 7, 142; Guye and Babel, *Arch. Sci. phys. nat. Genève*, 1899, [iii], 7, 23, 109), it appears to me advisable to give, in the following table, a *résumé* of the specific rotatory powers, $[\alpha]_D$, of these substances at the ordinary temperature (about 15° to 20°).

All the substances mentioned in this table are amyl derivatives, obtained by help of Claudon's primary active alcohol, having a specific rotatory power of $[\alpha]_D - 4.4^\circ$ to -4.5° . They may be divided into two groups:

(1) Mixed amyl ethers of the formula $C_5H_{11} \cdot O \cdot R$, in which R represents the radicles, phenyl, C_6H_5 , and *o*-, *m*-, or *p*-tolyl, C_7H_7 .

(2) Amyl esters of the formula $R \cdot CO \cdot O \cdot C_5H_{11}$, in which R represents phenyl (of benzoic acid), *o*-, *m*-, or *p*-toluyl (of toluic acid), benzyl (of phenylacetic acid), or phenylethenyl (of phenylpropionic acid, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO_2H$).

Substances.	$[\alpha]_D$.	Authors.
<i>First Group:</i>		
Phenyl amyl ether.....	+ 4.0°	Welt.
Benzyl „ „	1.82	Guye and Chavanne.
<i>o</i> -Tolyl „ „	3.9	Welt.
<i>m</i> -Tolyl „ „	3.9	„
<i>p</i> -Tolyl „ „	4.3	„
<i>n</i> -Butyl „ „	1.33	Guye and Chavanne.

476 OPTICAL ACTIVITY OF CERTAIN ETHERS AND ESTERS.

Substances.	$[\alpha]_D$.	Authors.
<i>Second Group :</i>		
Amyl benzoate	4.96°	Guye and Chavanne.
„ o-toluate	4.55	„ „
„ m-toluate	5.05	„ „
„ p-toluate	5.20	„ „
„ phenylacetate	3.84	„ „
„ phenylpropionate...	2.15	„ „
„ propionate	2.77	„ „
„ monochloracetate...	3.44	„ „

In order to show the analogy which exists between the rotatory power of substances containing the benzyl group, $C_6H_5 \cdot CH_2$, and compounds of the fatty series, data relating to *n*-butyl amyl ether have been inserted in the first group, and those relating to amyl propionate and amyl monochloracetate in the second. In this connection, it may be mentioned that *n*-butyl amyl ether and amyl propionate give the highest values for $[\alpha]_D$ among the homologous series of mixed amyl ethers, and among those of the amyl esters derived from fatty acids.

From the above figures, it appears that the benzyl radicle resembles the alkyl groups, C_nH_{2n+1} , rather than the phenyl, C_6H_5 , and toluyl, C_7H_7 , groups in the influence it exerts on rotatory power; this confirms the statements of Professor Frankland and his pupils.

It must be remarked, however, that this conclusion is only one case of the much more general statement already made in a recent paper (Guye and Babel, *loc. cit.*, p. 114; see also Tschugaeff, *loc. cit.*), namely, that when *substitutions of chains or groups of elements are effected in an asymmetric carbon compound in positions sufficiently far removed from the asymmetric carbon atom, the rotatory power is only slightly affected.*

This fact is clearly shown from the rotatory powers of benzoate, phenylacetate, and phenylpropionate of amyl. It is also to be noticed that the analogy existing between the rotatory powers of benzyl and acetyl derivatives is even more striking in the case of the compounds mentioned in the table than in that of the esters of tartaric acid studied by McCrae and Patterson. This is due to the fact that inasmuch as the latter contained two asymmetric carbon atoms, it is impossible to carry out a substitution which does not influence both of these atoms, and thus alter their optical powers algebraically; this may result in a specific rotation $[\alpha]_D$ in which the influence of the substitution may be hidden by the algebraic superposition of the optical powers of two asymmetric carbon atoms. It is sufficient to note that this point has already been treated of in detail in a previous publication (Guye and Babel, *loc. cit.*, p. 109, *et seq.*).