— 11·8°, and might prove identical in the same solvent; the sharpest test might be afforded by propylisopropylacetic acid.

9. *Steric Hindrance.—*The difference in the relative positions of atoms not only explains the different behaviour of optical antipodes, as has been indicated, but also gives some indication where no optical activity is concerned.

In the stereo-isomerism of ethylene compounds, taking maleic and fumaric acid as examples, space relations chiefly indicate that in one of the two the carboxyl groups CO2H are nearer. Such seems indeed to characterize maleic acid. It easily gives an an­

hydride of the cyclic formula

and, inversely, when cyclic

compounds such as benzene are broken down by oxidizing agents, it is maleic and not fumaric acid that appears. On the other hand the presence of the two negative carboxyls makes maleic acid the stronger acid but less stable, with a pronounced tendency to change over into fumaric acid; this goes hand in hand, according to a general rule, with smaller heat of formation, lower melting point and increased solubility.

In the cyclic compounds analogous phenomena occur. The for­mation of lactones, *i.e.* cyclic anhydrides derived from oxy-acids by interaction of hydroxyl and carboxyl, presents one of them. In the oxy-acids of the fatty series a particular feature is that from the isomers, denoted as α, *ß* and γ, &c. HO2C∙CHOH(CH2)nCH3, HO2CH2∙CHOH∙C(H2)n-1CH3,HO2C∙(CH2)2∙CHOH(CH2)b.2CH3, &c., the γ-compounds most easily form a lactone, though in the α-serics carboxyl and hydroxyl run nearer. The tetrahedral arrangement, how­ever, as shown in fig. 6, explains that A, one of the groups attached to the carbon atom C1, is fairly near C5, one of the groups attached to the carbon atom C4 (the angle A being 35°) ; A would correspond to the hydroxyl forming part of carboxyl around C1; C5 to the hydroxyl linked with the carbon atom in the γ-position.

A third consideration on analogous ground is that of “ steric hindrance.” It was introduced by Victor Meyer’s discovery that derivatives of benzoic acid, having two substituents (X and Ύ) in the immediate neighbourhood of carboxyl :—

are unable to form ethers in the ordinary way, by treating with methyl alcohol and hydrochloric acid, whereas the isomers having only one of the substituents Y in 4 (X in 6) readily do ; it was suggested that the presence of X and Y near CO2H prevented the access to the latter. This argument has not been completely established, but a large amount of quantitative corroboration has been brought to­gether by N. A. Menschutkin, who has found that in alcohols the more the hydroxyl group is surrounded by substituents (for instance CH3) the slower esterification (with acetic anhydride in acetone at 100°) takes place, the ratio of rates being

Methyl alcohol H3C∙OH . . 100

Ethyl alcohol H3C∙CH2∙OH . 48

Dimethyl carbinol (H3C)2CH∙OH . . 14

Trimethyl carbinol (H3C)3C∙OH . . 0∙8

*Stereo-isomerism in Other Elements.*

Phenomena analogous to those observed in carbon compounds might also exist in derivatives of other quadrivalent elements; and only the relative stability of carbon-compounds makes every form of isomer, which often is unstable, more easily obtainable in organic chemistry. Nevertheless it has been possible to obtain stereo­isomers with different elements, but, as expected from the above, especially in derivatives containing carbon. Some of them have the character of optical antipodes and are more easily considered from a theoretical point of view; others have not.

I. *Optically Active Stereo-isomers.—*-Most closely related to the phenomena with carbon are those with sulphur, selenium, tin and silicon, when these elements behave as quadrivalent. S. Smiles *(Journ. Chem. Soc.,* 1900, 77, pp. 1072, 1174; 1905, 87, p. 450)

split up such derivatives of methylethyl-thetine as

obtained by condensing methylethyl sulphide with ω-bromaceto- phenone, by means of the salt with *d*-bromocamphosulphonic acid, into optical antipodes.

W. J. Pope and A. Neville *(Journ. Chem. Soc.,* 1902, 18, p. 198) succeeded in the same way with a selenium compound

W. J. Pope and S. J. Peachey *(Journ. Chem. Soc.,* 1900, 16, pp. 42, 116) with a compound of tin (tin methylethylpropyl iodide)

Kipping *(Journ. Chem. Soc.,* 1904, 20, p. 15; 1907, 23, p. 9) with one of silicon (benzylethylpropyl silicol)

These facts may be explained in the same way as with carbon, by admitting tetrahedral grouping. A special feature, however, wanting with carbon, is that compounds with one atom only of the element in question have been obtained as antipodes. A second observation of some interest is that the compounds in question are electrolytes and that, as in solutions, where they are split up into ions, activity must be due to the last, the ionic complex, for in­stance, R1R2R3S̄, must cause optical rotation.

• Optical antipodes have also been obtained with quinquevalent nitrogen in compounds of the type: R1R2R3R4NR5. Le Bel observed these in methylethylpropyl-isobutylam monium chloride; since then Pope and Peachey and Wedekind studied the same question more thoroughly, and as a general result it is now stated that ammonium compounds with four different radicals behave as asymmetric carbon compounds. The explanation may be that the four radicals arrange themselves in the two possible tetrahedral configurations, and that the fifth element or group, *e.g.* chlorine or hydroxyl, more loosely linked, finds its fittest place, as shown in figs. 7 and 8.

2. *Stereo-isomers Without Optical Activity.—*The chief cases here belong to the derivatives of nitrogen with double linking and the metallic compounds which have been chiefly studied by Werner.

The nitrogen compounds showing stereo-isomerism belong to two classes, according to the structural formulae, containing C :N or N :N ; in their general behaviour they seem related to the ethylene derivatives.

The first group was detected by Victor Meyer and Goldschmidt in

benzildioxime :

Later investigations, especially by Hantzsch, showed that a grouping

gives rise to stereo-isomerism, the supposed difference being that X is either more close to R1 or to R2. This peculiarity is observed in the aldoximes and ketoximes, derived from aldehydes and ketones on treatment with hydroxylamine, and the two simplest examples are ethyl-aldoxime H3C·CH:NOH, and phenyl-benzyl-ketoxime, (C5H6) (C5H4CH2) C : NOH. As the behaviour of these stereo-isomers much resembles that of ethylene-compounds, they are often indi­cated as cis- and trans-forms.

The second stereo-isomerism in nitrogen-compounds was detected by Schraube in potassium benzenediazotate, and may perhaps be reproduced by the following symbols:—

The last group of stereo-isomers, in which insight is most difficult yet, is that of Werner’s complex metallic compounds, observed with cobalt, platinum and chromium. No. enantiomorphous character throws light here, and there is no relation to ethylene derivatives.

With cobalt the fact is that in the hexammonic cobalt salts, *e.g.* Co(NH3)5Cl3, when NH3Cl is substituted by NO2 isomerism appears as soon as the number of substituents is two; Jorgensen’s flavo-salts Co(NH3)4(NO2)2Cl, and Gibbs’s isomeric croceo-salts offer examples. Werner puts forward that a grouping of (NH3)5 at the summits of a regular octahedron around Co may explain this.