Polarimetric Methods in Chemistry*

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MUTAROTATION

NEARLY forty years ago, as a student of organic chemistry under Prof. H. E. Armstrong, I undertook my first research, on the stereochemistry of the α -derivatives of camphor. The earliest experiments showed that the bromination of α -chlorocamphor and the chlorination of α -bromocamphor both gave an isomorphous mixture of stereoisomeric $\alpha\alpha'$ - and $\alpha'\alpha$ -chlorobromocamphors. It was then natural to extend the research to the nitro-derivatives. For this purpose it was necessary not only to nitrate bromocamphor, but also to brominate nitrocamphor. In this way I first encountered the nitro-compound, $C_{10}H_{15}O.NO_2$, which has already provided a material basis for two extensive series of researches, and has not yet exhausted its utility or interest.

The first of a series of happy chances was a measurement of the optical rotatory power of a solution of nitrocamphor in the morning, followed by a confirmatory reading in the afternoon. During the luncheon interval the rotatory power of the solution had become quite different, and I was thus presented with a novel example of the phenomenon of change of rotatory power with time, which Dubrunfaut had first observed in 1846 in a freshly prepared aqueous solution of glucose. This property of the reducing sugars had been variously described as birotation, multirotation, and paucirrotation, according as the ratio of the initial to the final rotation was 2:1, greater than 1 or less than 1; but, since in certain solvents the *sign* as well as the magnitude of the rotation of nitrocamphor was changed, I suggested in 1899 that the phenomenon should be described as *mutarotation*; and this name has been in general use ever since.

The chemical basis of the phenomenon was disclosed by another happy accident. Wishing to know whether the change of rotatory power could be repeated when the nitrocamphor had been recovered from solution, I left a solution in benzene to evaporate on the water bath. Later in the day I examined the residue and found that it was now almost entirely insoluble in benzene. It had in fact been converted into a new compound, an anhydride formed from nitrocamphor by the loss of half a molecular proportion of water. An anhydride of this type could not be formed directly from nitrocamphor itself, but it could be derived easily enough from an isomeric hydroxylic

form of the substance, such as that from which the salts of nitrocamphor were presumably derived. This conclusion was confirmed by the fact that the anhydride of laevorotatory nitrocamphor was, like the salts, strongly dextrorotatory. The mutarotation of nitrocamphor, always from left towards right, could therefore be attributed to a partial conversion in solution of laevorotatory nitrocamphor into a dextrorotatory isomeride, containing an acidic hydroxyl group, which was capable of forming an anhydride as well as a series of salts.

At this stage, Prof. Kipping very generously gave me a quantity of the π -bromo-derivative of α -bromonitrocamphor, from which I was able to prepare a stock of π -bromonitrocamphor. Lapworth and Kipping had described this compound as trimorphous, and had recorded the crystal constants and published drawings of two of the forms. The orthorhombic form, melting at 142° , proved to be strongly dextrorotatory when dissolved in benzene, but it became laevorotatory after a few hours. The tetragonal form, melting at 108° (which is formed as a by-product, alongside the more stable form, by rapid evaporation of a solution in chloroform), was found to be laevorotatory, but like nitrocamphor it exhibited a relatively small mutarotation from left towards right. This labile form was therefore analogous with ordinary nitrocamphor, whilst the more stable form was analogous with the still unknown pseudo-nitrocamphor, the relative stability of the two isomers having been reversed by the introduction of a halogen. The third form, for which no crystal measurements had been published, was evidently a mere mixture of these two isomers.

The mutarotation of the sugars in aqueous solutions had been attributed to several causes; but, when Emil Fischer observed the same phenomenon during the reversible hydrolysis of the sugar lactones, he concluded that these changes of rotatory power were due to reversible hydration, and this conclusion was very widely accepted. This explanation can obviously be applied to any aqueous solution in which reversible hydrolysis can take place; but it was not applicable to nitrocamphor, which exhibited mutarotation in a large range of anhydrous solvents, but was too insoluble to be examined in aqueous solutions. Since interaction with the solvent was thus excluded, the mutarotation of nitrocamphor could only be attributed to *dissociation* or to *isomeric* or *polymeric change*.

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At that date, certain sugars had already been prepared in two isomeric forms, which exhibited mutarotation in opposite directions; but these changes were attributed to the complete conversion of the two sugars into a third isomeride. In the case of π -bromonitrocampafor, however, the product of mutarotation of the normal and pseudo forms was obviously an equilibrium mixture of these two substances, and not a third isomeride, since, on evaporation of the solution, crystals of the normal and pseudo forms were deposited side by side. Mutarotation was therefore attributed to the *reversible isomeric change* of two isomers; and this interpretation was regarded as generally applicable to mutarotations in which interaction with the solvent could be excluded.

DYNAMIC ISOMERISM

The phenomenon of reversible isomeric change had been studied, and its essential characteristics had been fully elucidated, twenty-two years before by Butlerow in 1877. He had shown that two isomeric forms of the unsaturated hydrocarbon, *isodibutylene*, C_8H_{16} , could be brought into equilibrium by the reversible addition of sulphuric acid, since a molecule of sulphuric acid could be removed from the acid sulphate in two different ways. Simultaneously, two *isodibutyl* alcohols of the formula $C_8H_{18}O$, in the form of their acid sulphates, were brought into equilibrium by the reversible elimination of sulphuric acid, since the resulting olefine could add on sulphuric acid in two different ways:

Butlerow also recognised that, although sulphuric acid was required to bring the isomeric olefines and alcohols into equilibrium, the introduction of a catalyst might not be required in other cases. In particular, he suggested that prussic acid might be regarded as an equilibrium mixture of the two acids, HCN and HNC, from which the cyanides

and *isocyanides* $CH_3.CN$ and $CH_3.NC$ are derived:

Methyl cyanide. Prussic acid. Methyl *isocyanide*.

Butlerow's paper did not receive the attention that it deserved, perhaps because it was published under the too modest title "*On Isodibutylene*". Much more interest was aroused by the publication, eight years later, by Laar, of a speculative paper "*On the Possibility of Several Structural Formulæ for the Same Chemical Compound*". Laar assumed that the dual reactivity of certain substances, of which ethyl acetoacetate is now the most familiar example, might be due to the incessant wandering of a hydrogen atom between two alternative positions in the molecule. In order to make his theory more precise, he compared these internal migrations with the vibrations which give rise to radiation in incandescent gases. To this phenomenon he gave the name of *tautomerism*, and in order to emphasise the contrast with Butlerow's phenomenon of reversible isomeric change, he stated categorically that the substances represented by the two alternative structural formulæ were "not isomeric but identical".

Since two isomeric forms of π -bromonitrocampafor had been isolated in the crystalline state, and their slow progress towards equilibrium in solution had been followed by observations of mutarotation, it would have been absurd to describe them as identical, or, in terms of Laar's definition, as tautomeric. These well-defined compounds, however, provided an excellent illustration of Butlerow's phenomenon of "equilibrium between isomers". I therefore ventured to describe this phenomenon in very obvious terms as *dynamic isomerism*, in contrast to the more usual condition of static isomerism, in which each isomer preserves its individuality and is not in process of conversion into any other substance of similar composition.

(To be continued.)

The Metamorphosis of Paper

ONE of the results of the application of scientific methods to the cellulose industries, and in particular to paper, has been a realisation of the considerable inherent strength of the unit fibre. One would, of course, hesitate to select paper for any purpose for which great strength is essential, but at the same time it must be remembered that, when paper is broken, it is usually the bonds connecting the fibres, and not the fibres themselves, which are ruptured. Reliable figures are necessarily difficult to obtain, but actual measurements indicate that, weight for weight, the tensile strengths of certain cellulose

fibres and of wires made from light metals are of the same order (cf. NATURE, 131, 553, April 15, 1933).

It is not unnatural, therefore, that many attempts have been made to produce paper products having the equivalent in strength and durability of more resistant materials such as cloth, leather, wood and even metal, and in such cases attention has usually been concentrated on strengthening the bonds between the fibres both laterally and longitudinally, on the reasonable assumption that the individual fibres can take care of themselves. By selecting the strongest of