Letters to the Editor

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A Correlation of the Walden Inversion with the Pinacone and Beckmann Changes

THE esterification of an alcohol may be represented as involving decomposition of an oxonium salt (I.), which corresponds closely to a reaction of quaternary ammonium hydroxides (II.):

These reactions very possibly proceed by extrusion of a molecule of water or tertiary amine, consequent upon attachment of anion in virtue of a positive charge on the carbon atom derived from, or induced by, that on the oxygen or nitrogen.¹ It may, however, be anticipated that this latter rather than the derived charge will determine the result, and permit only a condition of electrovalence, when the direction of approach of the anion is such as to expose it to the operation of either. In other words, covalent union with carbon will be dependent on approach from the side of the molecule remote from oxygen or nitrogen, and inversion of configuration must occur. As Kenyon and Phillips² have emphasised, inversion in general is associated with reactions of the type now discussed, but it is clear that similar considerations are applicable to a negatively charged atom and a cation, and it is probably only on account of the difficulty of realising these latter conditions in practice that Walden inversions of this type have not been realised.

The relationship of the Beckmann change to the Walden inversion is indicated by the facility of each type of change in the cases of the *p*-toluene sulphonic esters of oximes and alcohols respectively. Since, now, the behaviour of the oximes towards substituting agents is comparable with that of phenol,³ their isomerisation under the influence of strong acids may be attributed to formation of the system (III.):

The actual Beckmann change then represents an alternative possibility to the occurrence of depolarisation (by reversal of the initial change), which will be facilitated by the presence of a suitable anion to replace the migrating group X in its combination with the carbon atom. X in turn will promote detachment of hydroxyl or other ion from the nitrogen atoms. The analogy of this phase of the reaction to the changes referred to at the outset is obvious, and, accordingly, Meisenheimer's experiments⁴ have led him to conclude that inversion occurs, in the sense that it is X rather than Y which migrates. Corroborative evidence in favour of this view is afforded by another reaction, which has long been connected with

the Beckmann change, namely, the formation of amines from acid bromoamides and similar derivatives. The reaction is actuated by hydroxyl ions, and may thus reasonably be considered to be analogous in its first stage to the alkaline hydrolysis of esters,⁵ involving extrusion of the group X with the pair of electrons requisite to enable it to preserve its configuration⁶ and to displace bromide ion from the nitrogen atom:

As thus represented, the reaction is also not dissimilar from the benzylic acid change.

Like these, the pinacone and related changes also exhibit the characteristics requisite for an intramolecular Walden inversion, the negative change requisite for migration of the group R₂ arising from detachment of a proton from the hydroxyl group (or, in certain closely related changes, by attachment of an anion):

In this connexion, Kenyon and Phillips have already surmised that McKenzie's observations⁷ on the preservation of optical activity in these types of changes, and in semipinacolinic deamination, are indicative of a Walden inversion.

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¹ Compare NATURE, 128, 1000, Dec. 12, 1931.

² Compare J.C.S., 415; 1930: 382; 1931: Trans. Faraday Soc., 26, 451; 1930.

³ Charlton, Earl, Kenner, and Luciano, J.C.S., 30; 1932.

⁴ Ber., 54 B, 3206; 1921.

⁵ Compare Houben Weyl, "Methoden der organischen Chemie", 2nd ed., vol. 4, 339.

⁶ Jones and Wallis, J. Amer. Chem. Soc., 48, 169; 1926.

⁷ Compare, *inter alia*, Ber., 62, 272, 284; 1929.

X-Ray Interpretation of the Molecular Structure of Feather Keratin

SOME two years ago it was shown in this laboratory that the quill of a feather gives rise to a complex but well-defined X-ray fibre photograph¹ which is quite different from that of animal hairs.² It was afterwards shown that a similar photograph is given also by tortoise shell, and the conclusion was formed that it is characteristic of the keratin of feathers and reptilian scales as opposed to that of mammalian hairs, nails, horns, spines, etc.³ In the light of knowledge gained from the X-ray analysis of other protein fibres, it is now possible to interpret the feather photograph and fit it into the general scheme which such investigations, with increasing clearness, are beginning to unfold.

The details of the photograph need not be gone into here, and indeed have not yet been worked out completely, but it is clear now that it is only a rather bewildering elaboration of the type of photograph which is obtained from natural silk (fibroin)⁴ and the stretched form of hair (β-keratin),⁵ both of which have been referred to a polypeptide chain in a more or less fully extended state. The side spacings are similar, but there are indications of some ten hyperbolæ in the feather photograph. By the application of the principle of 'layer line enhancement',⁶ these may be separated into sets grouped round a chief