2-choro-5-nitro-, 2:4-dinitro-, 2:4:6-trinitrobenzaldehyde, or isatin, they were converted into acetaldehyde and benzaldehyde respectively.

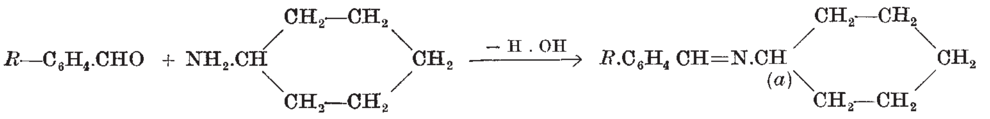
Although the interaction between *p*-hydroxybenzaldehyde and α-aminophenylacetic acid, in 75 per cent pyridine on a boiling water-bath for 3 hr., gave traces only of benzaldehyde, the yield greatly increased when the heating was carried out in boiling pyridine (3 hr.) or in quinoline at 160–170° for ½ hr. Under similar conditions, α-aminophenylacetic acid alone was not converted into benzaldehyde.

This showed that although a hydroxyl group is electron-repelling when attached to an aromatic nucleus, and, therefore, will inhibit the tendency for the decarboxylation of the azomethine carboxylic acid (I), yet the use of more drastic conditions (high temperature of the bath) facilitated the decarboxylation to the mesomeric anion (II).

When the hydroxyl group is attached to a saturated aliphatic chain, it acts as an electron-attracting group (I), and therefore it would be expected that saturated aliphatic hydroxyaldehydes, such as glyceraldehyde and glucose, are capable of effecting the degradation of α-amino-acids.

When α-amino-*m*-nitrophenylacetic acid was heated with *o*- and *m*-chlorobenzaldehyde in pyridine on the water-bath, it was partially converted into *m*-nitrobenzaldehyde.

When *o*-, *m*-, *p*-nitro- and *o*-, *m*-chlorobenzaldehyde were heated with alanine ester or α-aminophenylacetic ester in pyridine for three hours on a water-bath, practically no acetaldehyde or benzaldehyde, respectively, was obtained. Under similar conditions amines such as ethylamine, benzylamine and *cyclo*hexylamine were not converted into the corresponding carbonyl compounds (that is, acetaldehyde, benzaldehyde and *cyclo*hexanone, respectively). However, although stronger degrading agents such as isatin, 2 : 4-dinitro- and 2 : 4 : 6-trinitrobenzaldehyde were able to effect the conversion of ethylamine and benzylamine into acetaldehyde and benzaldehyde respectively, they failed to convert *cyclo*hexylamine into *cyclo*hexanone. This is an interesting result, since 1-amino-*cyclo*hexane-1-carboxylic acid is easily degraded to *cyclo*hexanone even with weak degrading agents such as *p*-nitro- and *o*-chlorobenzaldehyde[1b]. However, it may be due to the increase in the electron density created by the electron-repelling CH_2 groups on the carbon atom (*a*) of the azomethine (IV), which makes it very difficult to extract the proton from this carbon atom. Thus, no prototropic change will be possible under normal conditions.



IV

When *p*-hydroxybenzylidenebenzylamine was refluxed with pyridine for three hours, it failed to give any benzaldehyde. However, traces of it were obtained when the heating was carried out in quinoline at 160–170° for half an hour.

The above reactions were carried out in a carbon dioxide atmosphere, and when pyridine or quinoline was used as a medium, the reaction mixture was acidified with hydrochloric acid and the liberated carbonyl compounds steam-distilled.

A quantitative study of the extent of the prototropic change is now under investigation.

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Role of the Solvent in Reduction with Lithium Aluminium Hydride

Since the discovery of lithium aluminium hydride[1], it has been used for a variety of reductions[2]. Its reactions are normally those of hydride anions, and in the type of compound with which it reacts there is a far-reaching analogy with the Grignard reagent. The mechanism of the reaction has been investigated by Trevoy and Brown[3], who concluded from a wide range of evidence that the rate-determining step is a bimolecular nucleophilic substitution by a hydride ion, possibly complex.

This mechanism ignores the solvent, and it is the purpose of this communication to show that ether plays an essential part in the reaction, and to suggest how the above mechanism, which must be broadly true, may be modified to take account of its action.

The presence of ions in the ethereal solution of lithium aluminium hydride has now been proved directly; the specific conductivity of a molar solution was $(4 \cdot 43 \pm 0 \cdot 02) \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 15° C., which may be compared with that of a molar solution of ethyl magnesium bromide at 20° C. ($6 \cdot 14 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$)[4].

The reduction of three covalent halides, phosphorus trichloride, boron trichloride and silicon tetrachloride, was studied. The reaction of phosphorus trichloride with lithium aluminium hydride in ether is rapid below 0° C., and may be used to prepare phosphine in good yield. In the experiment reported here, phosphorus trichloride was heated under reflux in absence of ether for one hour at 75° C., with a 0·25 per cent yield of phosphine. Boron trichloride treated similarly gave no detectable quantity of volatile boron-containing material; on adding ether, a violent reaction to give diborane took place at the melting-point of ether. In another experiment, silicon tetrachloride heated under reflux with lithium aluminium hydride for one hour gave a negligible yield of silane. Ether was added at – 196° C., and as the temperature reached the melting point of ether a rapid evolution of silane (yield 96 per cent) ensued.

On the other hand, in qualitative experiments with acetone and benzonitrile (both compounds having donor properties), reduction took place without the addition of ether. The analogy with the Grignard reagent thus extends to the necessity for a donor solvent; evidence for a mono-etherate stable below 0° C. has been obtained.

As an explanation of the action of the ether, it is suggested that there is an equilibrium in solution :

$$AlH_4^- \rightleftharpoons H^- + AlH_3,$$

and that the function of the ether is to co-ordinate with the aluminium hydride and drive the equilibrium to the right-hand side. It is known independently that aluminium hydride retains ether tenaciously[1].

This explanation implies that the active entity is the H^- ion rather than the AlH_4^- ion ; this is being tested both by examining the effect of added aluminium hydride on the reactivity of lithium aluminium hydride solutions, and by transport experiments designed to determine the nature of the ions present.

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Intracrystalline Water in Pollucite

The natural mineral pollucite is generally formulated as $(Cs,Na)_2O.Al_2O_3.4SiO_2.H_2O$. It is isostructural with analcite, $Na_2O.Al_2O_3.4SiO_2.2H_2O$, both having cubic unit cells. Values of *a* reported for analcite range from $13{\cdot}6_5$ A. to $13{\cdot}6_7$ A. [1], and for pollucite from $13{\cdot}6_5$ A. to $13{\cdot}6_9$ A. [2].

The distribution of the water molecules in the pollucite structure raises an interesting point. According to W. H. Taylor[3], there are 24 available sites in the analcite unit cell for the 16 sodium ions, each sodium ion lying between four oxygen atoms of the framework and two water molecules. To preserve cubic symmetry, the sodium ions must be randomly distributed. The cations in the identical aluminosilicate framework of pollucite must be similarly distributed. The question then is whether the water molecules in the crystal are associated only with the sodium ions or may also be located in the vacant sites of the framework, of which there are just enough to accommodate the amount of water given in the above formula[1]. In order to decide this point, the following observations have been made.

The water content of some natural pollucites appears to decrease with decreasing sodium content and increasing cæsium content[4]. This suggests that the water may be associated only with the sodium ions ; but a final proof can be offered only by synthesizing a pure cæsium pollucite and demonstrating that it is anhydrous. This synthesis has now been carried out by us, using cæsium aluminosilicate gels in hydrothermal systems. (Details of the preparation of synthetic pollucites will be given elsewhere ; the mineral has also been grown by the recrystallization of chabazite[1].) The synthetic pollucite of composition $Cs_2O.Al_2O_3.4SiO_2$ has been found to be an anhydrous species. No water is then associated with the 8 vacant sites per unit cell. The correct formula for pollucite will then be $(Na_xCs_{1-x})_2O.Al_2O_3.4SiO_2.2xH_2O$.

The identity of the unit cell as between analcites and pollucites requires that, so far as occupation of the interstitial cavities in the identical aluminosilicate framework of these crystals is concerned, $(Na^+ + H_2O)$ is equivalent to Cs^+. By contrast, the anhydrous crystals in which, through ion exchange, the smaller units K^+, Rb^+ and Tl^+ replace $(Na^+ + H_2O)$ in analcite have slightly distorted anionic frameworks[1]. However, unlike sodium, rubidium and thallium ions, the cæsium ion is too large to migrate from one interstitial site in the crystals to the next, so that the framework exhibits an ion-sieve effect towards the cæsium ions, and this ion when incorporated during crystal growth is locked into the crystal[1]. The distribution of the 16 cæsium ions among the 24 equivalent sites per unit cell can be random in space but not in time. The mobile cations sodium, rubidium and thallium, on the other hand, may be randomly distributed in time and space. The size and immobility of the cæsium ions would then appear to explain the known difficulty in dehydration and rehydration of pollucites containing some sodium, when compared with analcite, since water molecules can escape from or enter the crystals only along the channels occupied by the cations. Dehydration of pollucite requires temperatures as high as 640° C. before completion, and rehydration involves heating the crystals in an autoclave with water at 400–500° C. [2].

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A Delicate Chromatograph Test for the Presence of Moisture in Alcohol

It has been found in this laboratory that paper-strip ascending chromatography affords a simple means of detecting small quantities of water (of the order of 0·1–5 per cent) present in alcohol.

The principle employed is to allow the alcohol to ascend a test paper strip (approximately 3/16 in. × 4½ in.) passing through two previously prepared zones, the lower being impregnated with iron sulphate and the upper with potassium ferricyanide. Neither of these salts is alcohol-soluble but both are water-soluble ; consequently, if the ascending alcohol contains water, iron sulphate will be eluted from the lower zone and carried to the upper, with the production of ferric ferrocyanide, visible as a band of Turnbull's blue. The extent and intensity of coloration depend on the amount of water present. If a pencil mark, say, 2 in. above the beginning of the upper zone, is used as the standard height of alcohol ascent, the method becomes quantitative after calibration runs with alcohol containing known amounts of added water.

At low concentration of water, the blue colour may not be apparent until the test-strip has been air-dried.

Of the various papers tried, 'Devon Mills' white blotting has been the most satisfactory. Solutions : lower zone, 3 per cent in water ; upper zone, 1 per cent in water.

Application is made with a glass tube of about ⅛-in. bore drawn down in a flame to give a smooth