Obviously this is an extravagant way which the plant would not take, but it involves certain types of reactions which have been studied in detail and indicates clearly the way in which such work may assist the "organic chemistry under biological conditions."

Our greatest difficulties up to the present time have been in securing in good yield certain of the basic substances in the synthesis of the amine (VII). The preparation of N-Methyl Isatin in large quantity had to be carefully worked out as the old Friedlander method does not give satisfactory results. Likewise the preparation of 1,3-Dimethyl Oxindole-3-Aldehyde (V) was secured in good yield only after numerous experiments. We have not yet been successful in obtaining smooth ring closure to (IV) but hope to report success in this direction when the complete experimental results are published. Our purpose in this review has been largely to stimulate interest in such work by reviewing briefly our own experiences and those of others.

SEPARATION OF IRON FROM INDIUM WITH CUPFERRON

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Experiments conducted some years ago upon the methods for the separation of iron from indium showed this separation to be difficult and unsatisfactory by any of the methods and they led to a new method based upon the precipitation of the iron with nitroso-B-naphtho[1]. More recently the use of cupferron as a reagent for the precipitation of iron, suggested the idea that it might be substituted advantageously for the nitroso-B-naphthol. Experiments by various authors[2] have shown that a six per cent solution of cupferron will completely precipitate iron, copper and certain other metals in hydrochloric acid solutions while aluminum remains in solution. Indium is so closely related to aluminum in the Mendeleeff Periodic Table that a similar behavior towards cupferron was to be expected.

Preliminary experiments with the cupferron method for precipitating iron showed that an error of 0.4 to 0.8 mg. was made when using 0.07 g. Fe_2O_3 as ferric chloride, 0.7 g. cupferron and 1 to 3 cc. of hydrochloric acid, in a total volume of 40 cc. Portions of an indium chloride solution to which portions of a standard ferric chloride solution were added, were precipitated with cupferron. The precipitates were ignited and weighed as ferric oxide (Fe_2O_3). The filtrates were precipitated with ammonium hydroxide and the residues thus obtained were ignited

[1] Mathers, This Jour., 30:209 (1908).

[2] Fresenius, Z. anal. Chem., 50:35 (also a review with references). Becculi and Grassi, Gazz. chim. ital., 43 I 570; through C. A. 7:1688.

Thornton, Am. J. Sci., (4) 37:137 and 407.

over Bunsen burners and weighed as indium oxide (In_2O_3). This residue of indium oxide showed from 0.07 to 0.12 mg. of ferric oxide (Fe_2O_3), the test being made by color comparison using potassium sulphocyanate.[3] The following table shows the results:

No.	In_2O_3 taken (g.)	Fe_2O_3 taken (g.)	HCl added (cc.)	Cupfer. added (g.)	Final volume of sol. (cc.)	Fe_2O_3 ppt. by cupfer. (g.)	In_2O_3 from filtrate (g.)	In_2O_3 lost (g.)
1	0.0606	none	2	0.24	16	0.0025	0.0598	0.0008
2	0.0606	0.0363	3	0.60	21	0.0387	0.0598	0.0008
3	0.0606	none	3	0.24	17	0.0009	0.0586	0.0020
4	0.0606	0.0726	3	0.60	33	0.0760	0.0587	0.0019
5	0.0606	0.0726	3	0.60	33	0.0721	0.0603	0.0003
6	0.0718	none	3	0.24	17	0.0018	0.0695	0.0023
7	0.0718	none	3	0.24	17	0.0009	0.0698	0.0020
8	0.0718	0.0726	3	0.60	33	0.0726	0.0690	0.0028

The method of Gooch and Havens[4] for the separation of aluminum from iron was tried for indium and iron. This method is based upon the fact that hydrous aluminum chloride ($AlCl_3.6H_2O$) is insoluble in a mixture of strong hydrochloric acid and ether saturated with hydrochloric acid gas, while ferric chloride is completely soluble. This method, tested with standard solutions of aluminum chloride and varying amounts of ferric chloride, showed an error on the aluminum of —0.2 to —0.8 mg. After this proof that the operation of the method was understood, experiments were undertaken with indium chloride solutions. In no case was it possible to obtain a precipitate of the indium chloride. The conditions were varied and a number of other organic liquids, e.g., chloroform, glacial acetic acid, and carbon tetrachloride, were tried, but no precipitate was obtained. The conclusion must be drawn that the properties of the elements of group III vary with increasing atomic weight to such an extent that the indium chloride is soluble although the aiuminum chloride is insoluble in a mixture of ether and hydrochloric acid saturated with hydrochloric acid gas.

SUMMARY

1. Cupferron will completely precipitate iron in the presence of indium.

2. There is a small loss in the quantity of indium. The cause of this loss was not investigated.

3. The precipitate of the iron with the cupferron filters easily and is not bulky like the precipitate with nitroso-B-naphthol, hence material containing a larger quantity of iron may be treated.

4. This method is considered the best for the complete purification of indium from small amounts of iron. The major portion of the iron should be removed previously by some other method[1].

[3] Schaeffer, J. Ind. Eng. Chem., 4:659 (1912).

[4] Am. J. Sci., (4) 2:416 (1897).

5. Indium chloride is soluble in a mixture of ether and strong hydrochloric acid saturated with hydrochloric acid gas, consequently the method of Gooch and Havens for the separation of aluminum and iron cannot be applied to indium and iron.

THE SECONDARY REACTIONS IN THE PREPARATION OF ZINC ETHYL

RUSH F. MCCLEARY[1] and ED. F. DEGERING

In 1849 in his research on free radicals, Frankland (1) treated zinc with ethyl iodide in a sealed tube at 150° C. As products of the reaction, he obtained a gas mixture, crystals of ethyl zinc iodide, and a clear liquid, zinc ethyl. His analysis of the gas gave 50.03 per cent butane, 25.79 per cent ethane, 21.7 per cent ethylene, and 2.48 per cent nitrogen. But neither Frankland nor subsequent workers have offered a satisfactory explanation of the mechanism of this reaction.

Various theories have been proposed to explain reactions of this type. Nef[2] proposed alkylidene dissociation, and produced experimental data for the Würtz reaction which indicated that sodium reacts with ethyl iodide to give 50 per cent butane, 25 per cent ethane, and 25 per cent ethylene. But alkylidene dissociation should also foster the formation of some butylene, and the relative quantities of the products formed if the alkylidene radical is the active intermediate in reactions of this type can be shown to be x mols of ethylene, y mols of butylene, $(x + 2y)$ mols of ethane, and z mols of butane. Expressed in equation form,

$$2(x+2y+z)CH_2CH_2I + \text{dissociation} \rightarrow 2(x+2y+z)CH_3.CH\rightleftarrows^{3} + 2(x+2y+z)HI$$
$$2(x+2y+z)HI + 2(x+2y+z)Na \rightarrow 2(x+2y+z)NaI + 2(x+2y+z)H$$
$$xCH_3.CH\rightleftarrows + \text{rearrangement} \rightarrow xH_2C{:}CH_2$$
$$yCH_3.CH\rightleftarrows + yCH_3.CH\rightleftarrows \rightarrow yCH_3.CH{:}CH.CH_3$$
$$(x+2y)CH_3.CH\rightleftarrows + 2(x+2y)H \rightarrow (x+2y)CH_3.CH_3$$
$$2zCH_3.CH\rightleftarrows + 2zH \rightarrow zCH_3.CH_2.CH_2.CH_3$$

However, these relationships are not satisfied by the data of either Frankland or Nef, which indicates either a faulty theory or faulty data.

Another theory that has been advanced to interpret reactions of this type is disproportionation. Experimental data seem to indicate that disproportionation reactions may involve either molecules or radicals or both, as illustrated by the following equations:

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[1] Abstract of a thesis presented to the faculty of Purdue University by Rush Fox McCleary in partial fulfillment of the requirements for the degree of Master of Science.

[2] Data obtained from lecture notes of Dr. F. W. Upson, student of J. U. Nef.

[3] Free radicals are indicated by use of arrows.