6. It was observed that the abietates of the heavy metals were quite soluble in non-aqueous solvents and insoluble in water.

In conclusion, the writer takes this opportunity to thank Professor Kahlenberg for his valuable suggestions offered during the progress of the work.

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THE USE OF PYRIDINE AS A SOLVENT IN THE ESTIMATION OF HYDROXYL GROUPS BY MEANS OF ALKYL MAGNESIUM HALIDES.

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During the past eight or nine years there have been published a number of articles dealing with a method for the determination of hydroxyl groups in organic compounds by means of the Grignard reagent. The reaction involved, discovered by Grignard and Tissier,[1] and first developed qualitatively by Tschugaeff,[2] is as follows:

$$R.MgX + R'.OH = R.H + R'.OMgX.$$

In the methods proposed for the quantitative estimation of hydroxyl groups, the substance is dissolved in some solvent and the solution mixed with a solution of CH_3MgI in amyl ether, with a resultant evolution of methane, the volume of which is measured. From this volume can be readily calculated the number of hydroxyl groups in the molecule.

It is necessary, in carrying out a determination, to avoid all traces of moisture in the apparatus and in the reagents used. A more troublesome difficulty arises in connection with the use of a suitable solvent. The requirements in this direction call for, first, low vapor pressure; second, ease of purification; and third, general applicability.

Ethyl ether, the solvent used by Tschugaeff,[3] is useless for quantitative purposes on account of its very high vapor pressure. The first investigators to apply the method to quantitative purposes were Hibbert and Sudborough, who used amyl ether and phenetole with partial success.[4] These two solvents met admirably the first two requirements named above, but their application was not sufficiently wide, and it was shown that while very accurate results were obtained in many determinations, amyl ether solutions of the aliphatic amines and the lower fatty alcohols gave abnormal results, while phenetole solutions of almost all hydroxyl compounds and amines gave low results.

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[1] *Compt. rend.*, **132**, 835 (1900).

[2] *Ber.*, **35**, 3912 (1902).

[3] *Loc. cit.*

[4] Hibbert and Sudborough, *J. Chem. Soc.*, **85**, 933 (1904); Sudborough, *Ibid.*, **95**, 477 (1909); Hibbert, *Ibid.*, **101**, 328 (1912).

In investigating the efficiency of the method using pyridine as a solvent, Zerewitinoff[1] obtained normal results with aromatic and aliphatic hydroxyl compounds and amines, including the lower fatty alcohols, the figures in many cases showing a deviation from the theoretical which was surprisingly small, if one bears in mind the comparatively high vapor pressure of pyridine, and the fact that Zerewitinoff used and recommends *technical* pyridine as a solvent, and carried out most of the determinations in air, which is absorbed by CH_3MgI.

In view of the advantages which this author claims for the method, it seemed advisable to try out pyridine as a solvent. The results obtained, however, were very unsatisfactory. Thus, with α-naphthol over twice the theoretical amount of gas was evolved. Since the α-naphthol was of known purity, it was decided to investigate the action of pyridine alone on CH_3MgI. The pyridine used in these preliminary determinations was a high-grade technical pyridine obtained from the Baker & Adamson Company, dried over barium oxide as directed by Zerewitinoff. In a number of blank determinations a considerable amount of a gas, presumably methane, was evolved.

In order to find the source of trouble, the apparatus was first tested out by making a blank determination with amyl ether dried over sodium. There was absolutely no change in volume on mixing the amyl ether with the CH_3MgI, and the difficulty was therefore narrowed down to the pyridine itself, or to impurities which it contained other than moisture.

The following series of determinations was therefore carried out, using various samples of pyridine (described below), and using in all cases an excess of the Grignard reagent. The determinations were carried out at room temperature, and it should be emphasized that in each case the evolution of gas was immediate.

Solvent.	Amount of solvent used. Cc.	Amount of CH_3MgI solution used. Cc.	Volume of gas evolved reduced to N. T. P. Cc.
Pyridine I	15	10	38.5
Pyridine II	10	5	60.9
Pyridine III	10	5	27.6
Pyridine III	10	5	29.2

Pyridine I was a sample obtained from Kahlbaum, further purified by fractional distillation and by boiling over barium oxide for twenty-four hours.

Pyridine II was another sample of Kahlbaum pyridine, boiling point 115–117°, dried over barium oxide.

Pyridine III was obtained from the Baker and Adamson Company. It was guaranteed to be free from ammonia, and boiled between 116 and 118°.

The pyridine used in these determinations was carefully protected from moisture throughout the process of purification. All apparatus used was dried for one-half hour at 110°, rinsed out with a current of dry air, and

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[1] *Ber.*, 40, 2023 (1907); 41, 2233 (1908); 43, 3590 (1910); 45, 2384 (1912).

kept in a desiccator until used. All the determinations were carried out in an atmosphere of dry nitrogen. The apparatus used was similar to that described by Zerewitinoff, and the magnesium methyl iodide was prepared in accordance with his directions.

No attempt was made to explain the results given in the above table, which differ so strikingly from those obtained by Zerewitinoff. It is certain, however, that the pyridine used was of a higher grade of purity than the technical pyridine which he used, and it was at least as dry. The fact that Oddo[1] obtained satisfactory results by its use may be due to the fact that he employed magnesium ethyl iodide.

In conclusion, attempts to utilize pyridine as a solvent in accordance with Zerewitinoff's directions have failed completely from a quantitative point of view, not only with the technical product but with the repurified Kahlbaum material. Even with added precautions, pyridine has not been found to be a suitable solvent for use in this method; and it would therefore seems advisable that this method be subjected to further investigation before results obtained by its use are accepted.

The author wishes to acknowledge his indebtedness to H. Hibbert, at whose suggestion this work was undertaken.

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[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE ORIGIN OF PURINES IN PLANTS.[2]

BY TREAT B. JOHNSON.

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In the plant kingdom purines occur as normal constituents of the plant cell, linked to sugar in the nucleic acids, and also in a free condition as stable end products of the metabolism of nitrogen. They are found in certain plants associated with protein in all the organs, apparently, in which protein is synthesized or utilized in plant growth. Regarding the mechanism of the processes of formation, or the chemical nature of the simpler organic compounds, which participate in their syntheses, we have, however, practically no knowledge. The primary object of this paper is to present some interesting data, which are very suggestive of the mechanism of purine formation, and which have led us to undertake some new investigations in this fruitful field.

Every process, which has been applied successfully in the laboratory, for the synthesis of purine compounds, is based upon the general principle that the imidazole ring can be introduced into the pyrimidine nucleus.

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[1] *Ber.*, 44, 2040 (1911).

[2] Pyrimidine Paper LXV.