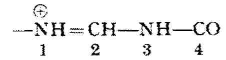
Table IV

Assay of Variouy Hydrochlorides for the Presence of "Immonium Bands"

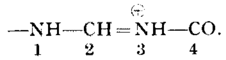
Compound (measured in C = Chloroform, or N = Nujol)	Immonium Bands
Nicotine monohydrochloride (Fig. 1 (C)	–
Nicotine dihydrochloride (Fig. 1) (C) . .	4·77^{m}; 5·05^{m}
Peganine (vasicine) hydrochloride (N) .	–
Pegadiene hydrochloride (C)	–
4-Quinazolone hydrochloride (N)[a] . . .	4·92^{vw}; 5·30^{vw}
Febrifugine dihydrochloride (N)[a] . . .	4·86^{w}; 5·14^{m}; 5·43^{m}

[a] It was expected that the weakly basic character of the amide nitrogen in position 3 would restore the independence of the cation



$$\overset{\oplus}{\underset{1}{-NH}}=\underset{2}{CH}-\underset{3}{NH}-\underset{4}{CO}$$

by suppressing the contribution



$$\underset{1}{-NH}-\underset{2}{CH}=\overset{\oplus}{\underset{3}{NH}}-\underset{4}{CO}.$$

Such an effect is operative and leads to the appearance of immonium bands, very weak in quinazolone hydrochloride, more distinct in the dihydrochloride of the quinazolone alkaloid febrifugine (an alkaloid from Hydrangea, *cf.* B. R. Baker, *et al.*, J. Org. Chem. *17*, 132 [1951]; I am greatly indebted to Dr. Baker for samples), where there must be bonded or non-bonded interaction between the three oxygen functions: desoxyfebrifugine dihydrochloride, where no such interaction is possible, lacks immonium bands.

immonium bands is unexpected and might be due to the direct or, less likely, vinylogous attachment of N^b to the $>C=N^a-$ group, in other words, an α-aminoindolenine type of structure (I). The substantiation of this concept is awaiting further chemical experiments. A full report on further uses of the immonium bands for diagnostic purposes (positional effect of alkyl substituents in pyridines and quinolines, shift to longer wave length in aromatic N-oxide hydrochlorides, ketimine-enamine tautomerism, etc.) will appear in the near future[1].

B. Witkop

National Institutes of Health, Washington 14, D.C., February 8, 1954.

Zusammenfassung

Bei der Salzbildung offener oder zyklischer Schiffscher Basen, eingeschlossen aromatische Heterozyklen, wie Pyridin, Chinolin, Benzoxazin, Indolenin usw., können die im UV.- und UR.-Spektrum auftretenden batho- oder hypsochromen Verschiebungen sowie das Auftreten oder Ausbleiben der für das Kation $>C=\overset{\oplus}{N}H-$ charackteristischen «Immonium-Banden» bei 4,5–5,5 μ zur Erkennung der Natur und der Position von Aminosubstituenten benutzt werden.

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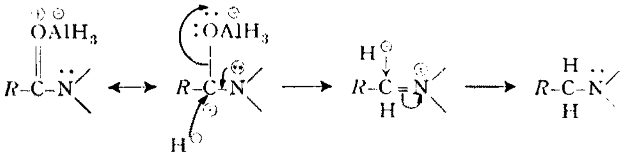
[1] The method has been utilized to advantage in the meantime: the tobacco alkaloid myosmine was found to be a Δ_1-pyrroline derivative as the free base as well as in the form of the mono- and dihydrochloride, B. Witkop, J. Amer. Chem. Soc. *76*, in press. Likewise, new structures had to be postulated for tetrahydropyridine and γ-coniceine (added in proof).

The Reduction of Amides with Lithium Aluminium Hydride[1]

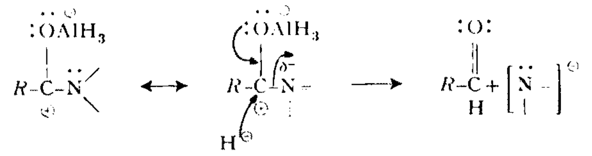
The reduction of carboxylic acid amides with lithium aluminium hydride generally yields the corresponding amine with the same number of carbon atoms[2]. However, in some cases, amides are cleaved to alcohols or aldehydes and amines[3].

The following mechanism has been proposed[4] for the reduction of amides and vinylogs of amides to yield the corresponding oxygen-free compounds:



The reactive species here is the aluminohydride ion $AlH_4^{\ominus}$ which, according to Paddock[5], exists in ether solution in equilibrium with aluminium hydride and the hydride ion. The attack of the hydride ion and the tendency of the nitrogen atom to donate its electron pair to the electron deficient carbon results in a cleavage of the carbon-oxygen bond to yield the amine, with a total consumption of one-half mole of lithium aluminium hydride.

When the electron-donating tendency of the nitrogen atom is decreased by stabilization, the adjacent carbon assumes a more positive character. The attack by the hydride ion alone or in conjunction with a shift of electrons from the oxygen atom results in a cleavage of the carbon-nitrogen bond to yield the carbonyl derivative and the starting amine.



The isolation of aldehydes generally requires the addition of one-quarter mole of lithium-aluminium hydride to a solution of amide. These conditions are fulfilled by the indicated mechanism. The aldehyde therefore does not arise as a result of the hydrolysis of an intermediate complex, as has been postulated[6], but is present in the reaction mixture prior to hydrolysis. The use of excess complex hydride causes a reduction of the aldehyde to the corresponding alcohol.

The mechanism has been experimentally verified. The benzamide of benzotriazole was treated with one-quarter mole of lithium aluminium hydride in ether, with inverse

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[1] Contribution No. 13 from the Yerkes Research Laboratory.

[2] R. F. Nystrom and W. G. Brown, J. Amer. Chem. Soc. *70*, 3738 (1948). – A. Uffer and E. Schlittler, Helv. chim. Acta *31*, 1397 (1948).

[3] K. Banholzer, T. W. Campbell, and H. Schmid, J. Amer. Chem. Soc. *35*, 1577 (1952). – G. Wittig and P. Hornberger, Ann. Chem. *577*, 11 (1952). – N. G. Gaylord, J. Amer. Chem. Soc. *76*, 285 (1954). – V. M. Mićović and M. L. Mihailović, J. Org. Chem. *18*, 1190 (1953). – M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, Bull. Soc. chim. France [5] *19*, 1042 (1952).

[4] N. G. Gaylord, Exper. *10*, 166 (1954).

[5] N. L. Paddock, Nature *167*, 1070 (1951).

[6] V. M. Mićović and M. L. Mihailović, J. Org. Chem. *18*, 1190 (1953). – M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, Bull. Soc. chim. France [5] *19*, 1042 (1952).

addition. The infrared spectrum of a sample of the reaction mixture, withdrawn before hydrolysis, indicated a strong absorption at 5·85 μ, and was identical, over the range 5·75–6·00 μ, to the spectrum obtained from a synthetic mixture containing benzotriazole, the benzamide of benzotriazole, benzaldehyde and ether, and was different from that obtained from the synthetic mixture in the absence of benzaldehyde. The reduction products, after hydrolysis and the usual work-up, were benzaldehyde and benzotriazole. It has previously been reported that the reduction of the benzamide of benzotriazole with excess lithium aluminium hydride yields benzyl alcohol and benzotriazole[1].

A nitrogen-aluminium bond has been postulated as an intermediate in the cleavage of compounds containing the $-\ddot{\underset{\cdot\cdot}{N}}-\overset{|}{\underset{|}{C}}-\ddot{\underset{\cdot\cdot}{O}}-$ grouping[2]. The failure to form an oxygen-aluminium bond in such compounds may be due to the non-polarizability of this carbon-oxygen bond.

N. G. Gaylord

Yerkes Research Laboratory, Film Department, E. I. du Pont de Nemours and Company, Inc., Buffalo 7, N.Y., June 30, 1954.

Zusammenfassung

Ein einfacher Mechanismus wurde vorgeschlagen und ein experimenteller Beweis gegeben, um die Bildung von Aminen oder Abspaltungsprodukten in der Reduktion von Amiden mit Lithiumaluminiumhydrid zu erklären.

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[1] N. G. Gaylord, J. Amer. Chem. Soc. *76*, 285 (1954).

[2] N. G. Gaylord, Exper. (in press).

Infra-red Study of the Carbonate in Bone, Teeth and Francolite[1]

Introduction

One of the major problems in the crystallography of the inorganic portion of teeth and bone, as well as the mineral francolite, is the elucidation of their carbonate content. Many investigators have claimed that the carbonate is found as an amorphous calcium and magnesium carbonate physically mixed with the apatite phase of these substances[1]. There are others who believe that a carbon radical substitutes in some way, in a structural position of the apatite, forming a carbonate-bearing member of the apatite series[2].

The amount of carbon dioxide released by treating these materials with acid is by no means a trace amount. In the four samples studied, we have the following analyses based on samples purified by specific gravity separation and dried at 110°C. (It is well to note that the bone, dentine and enamel were freed of organic material by boiling in a solution of KOH in glycerine according to the method of Gabriel[3].)

Sample	% CO_2
cow enamel	2·88
cow dentine	3·91
cow bone (femur)	5·15
francolite	2·70

X-ray work

It is evident that if the CO_2 were present as well crystallized $CaCO_3$ and $MgCO_3$, it would be possible to see the lines of these materials by X-ray diffraction. In fact it was demonstrated that it is possible to detect as little as 3% $CaCO_3$ admixed with apatite by X-ray diffraction methods[4]. However, the latter proof depends upon well crystallized calcite and in the case of the materials studied, it is postulated that the carbonates are too finely crystallized to be detected by X-ray

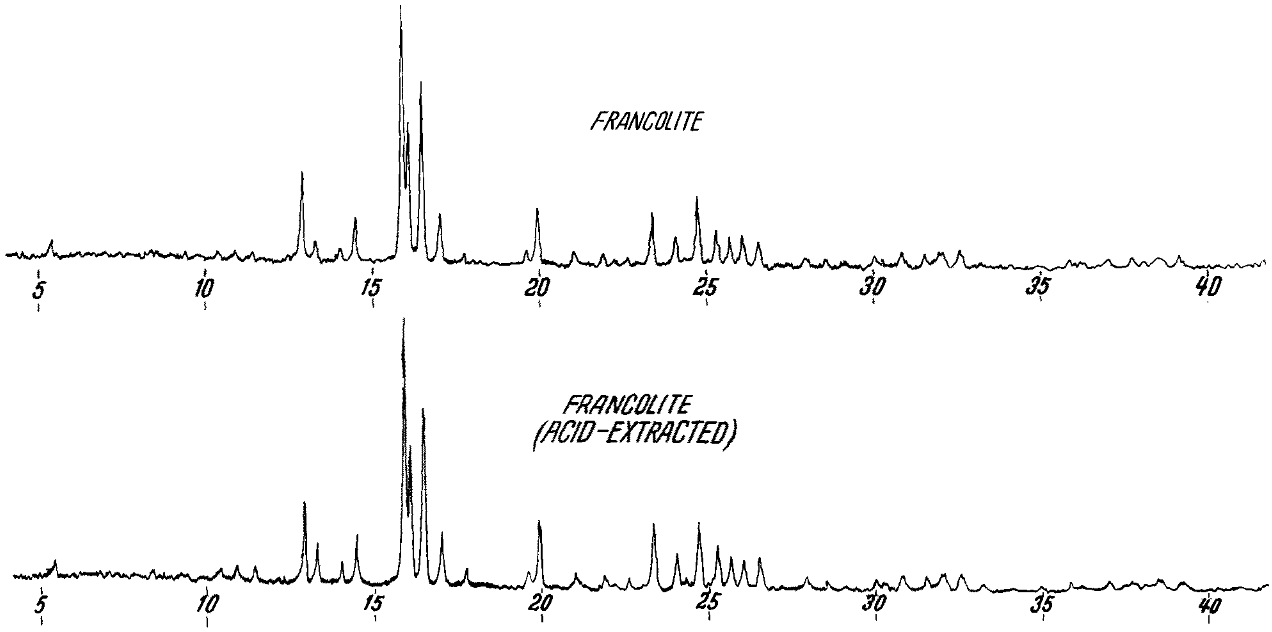

Fig. 1.–X-rays patterns taken with Copper K-alpha radiation. Angles given in degrees theta (Θ).

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[1] This work was partially sponsored by the *Air Research and Development Command*, United States Air Force, through its European Office under contract n° AF 61 (514) 647 C.

[1] W. F. Bale, Amer. J. Roentgenology *95*, 735 (1940). – M. L. Le Fevre, W. F. Bale, and H. C. Hodge, J. Dent. Res. *16*, 85 (1937). – G. Trömel and H. Möller, Z. anorg. allgem. Chem. *206*, 227 (1932). – M. J. Dallemagne, J. Physiol. *43*, 425 (1951).

[2] D. McConnell and J. W. Gruner, Amer. Min. *25*, 157 (1940). – D. McConnell, Bull. Soc. franç. Minéral. Crist. *76*, 428 (1952).

[3] S. Z. Gabriel, Z. physiol. Chem. *18*, 257 (1894).

[4] S. R. Silverman, R. K. Fuyat, and J. A. Weiser, Amer. Min. *37*, 211 (1952).