DIPYRIDINE TRIMETHYLENE DIBROMIDE, AND A STUDY OF CERTAIN ADDITIVE REACTIONS OF ORGANIC BASES.[1]

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IN the course of an inquiry into certain limits to the formation of the addition compounds of amines with halogen substituted hydrocarbons, an inquiry made both historically and by experimentation, the compound named first above was obtained. In this study the bases chiefly considered are the tertiary amines, and the halogen compounds chiefly those of mono- and dihalogen substitution, especially in the saturated hydrocarbons.

ALKYL HALIDES IN THE FORMATION OF NITROGEN BASES.

Among the more simple aliphatic bases, it is obvious that there are limits (other than those of valence) to the concentration of carbon, or displacement of hydrogen, in the atomic positions next but one to the nitrogen.[2] Among well known products, normal propyl forms a primary, a secondary, and a tertiary amine, likewise a quaternary[3] base iodide, and hydroxide, the latter not decomposed at 100° C. In contrast, isopropyl has been found to form only a primary and a secondary amine. The butyls, as base-forming alkyls, behave with a like gradation of formative power. Normal butyl holds the four ammonium valencies of nitrogen.[4] Isobutyl, primary, forms the quaternary base iodide,[5] but not bromide.[6] Secondary butyl forms the secondary amine but sparingly, the tertiary with difficulty, and this refuses to unite with iodide of the same alkyl in formation of a quaternary base.[7] Finally the tertiary butyl appears to form only a primary amine, namely, trimethyl carbinamine, $(CH_3)_3CNH_2$.[7]

This was obtained by Butlerow,[8] as a bye-product, from tertiary butyl cyanide, during the conversion of this nitrile to tri-

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[1] Read at the Springfield Meeting of the American Association for the Advancement of Science.

[2] That is, as atoms directly linked to *alpha* C.

[3] H. Roemer, 1873: *Ber. d. chem. Ges.*, 6, 1101.

[4] Lieben and Rossi, 1873: *Ann. Chem.* (Liebig), 165, 109.

[5] Sachtleben, 1878: *Ber. d. chem. Ges.*, 11, 733.

[6] Reimer, 1870: *Ber. d. chem. Ges.*, 3, 756.

[7] S. Reimann, 1874: *Ber. d. chem. Ges.*, 7, 1289.

[8] *Ann. Chem.* (Liebig), 170, 151; 162, 7, 12.

methyl acetic acid, and has been obtained, as stated, through transformation of isobutyl iodide, when acted upon by silver cyanide, by Linnemann,[1] and by Brauner.[2] Rudneff,[3] also has studied trimethyl carbinamine. The last named chemist found that although trimethyl carbinamine unites with tertiary butyl iodide to form the secondary base in its hydriodide, $(CH_3)_3C_2NH.HI$; on distilling this with potash the secondary amine was not formed, but only the primary amine again. This boils at 45° C. The preparation of trimethyl carbinamine by transformation of isobutyl iodide in reaction with silver cyanate, as reported by Linnemann,[4] was tried by A. W. Hofmann, in 1874,[5] without success, obtaining chiefly isobutylamine, after which Brauner, at Linnemann's request, went over the work with great care, and has reported the operation with his interpretation of the reaction and his successful production of the primary amine of the tertiary alkyl, as above cited. He obtained, however, both isobutylamine and the tertiary butylamine. In repeating his operation twice, the second time with rigid rectification of materials and products, we obtained the hydrochloride of a base which agrees in centesimals with a pure butylamine. On distilling this over potassium hydroxide, no distillate was obtained of a boiling-point below 65° C. The first distillate had just the boiling-point of isobutylamine, primary amine of primary alcohol, a result which only gives to us another indication that tertiary alkyls do not form amines with readiness.

The greater avidity of methyl halides than of ethyl halides, in additive reaction with tertiary bases, is a common laboratory observation. This difference, however, cannot be attributed wholly to the ratio of hydrogen carried by the carbon atom linking to nitrogen, because of the higher ratio of total hydrogen to total carbon in the methyl as compared with entire ethyl. But the disparity in reactive strength between propyl and isopropyl can be theoretically attributed to the one difference between the two alkyls, the structural difference in ratio of hydrogen to car-

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[1] 1872: *Ann. Chem.* (Liebig), **162**, 19.

[2] 1878: *Ann. Chem.* (Liebig), **192**, 65.

[3] 1878: *Ber. d. chem. Ges.*, **11**, 988, 1938; **12**, 1023; 1880. Bull. Soc. chim., [2], **33**, 297.

[4] Already cited. This transformation agrees with that of isobutyl alcohol into trimethyl carbinol, reported at the same time by Linnemann: *Ann. Chem.* (Liebig), **162**, 12.

[5] *Ber. d. chem. Ges.* **7**, 508.

bon in positions nearest the nitrogen. In speed of additive reaction toward triethylamine, Menschutkin[1] found that of normal propyl iodide to be 0.0116, that of isopropyl iodide to be 0.00121, in like measures of the two. Normal butyl was to isobutyl as 0.00832 to 0.00191. Ethyl to normal propyl as 0.00584 to 0.000984, all the alkyls acting as iodides, the reactions being compared in the same solvent. In recent studies[2] of the same investigator, tertiary amines are compared with secondary and primary amines in speed of additive reaction with the same alkyl bromide, in each of four series. Toward methyl bromide, diethylamine is to dipropylamine, as 16886 to 10264; toward ethyl bromide, the same amines, respectively, as 182 to 101, in speed of addition. Using electrolytic measurement of the affinity coefficients, Bredig[3] finds the quaternary organic bases to be the strongest and the tertiary the weakest, each taken in its ammonium chloride.

The limits of the addition of aliphatic tertiary bases, those of simple composition, to halogen substituted hydrocarbons, have been lately studied by Kleine,[4] the chief question being the additive capacity of a secondary, and a tertiary, halogen substituted group. The bases studied were trimethylamine and triethylamine: the halides were monobromine and dibromine substituted hydrocarbons in the saturated series as far as pentane, as well as various unsaturated derivatives of open carbon chain. It was concluded by Kleine, from work previously reported and from some work of his own, that addition is not effected with the linking group CHX (X being the halogen), nor with a tertiary group CX, nor if a secondary or tertiary substituted group be present in the compound. Addition is not obtained with ethylidine bromide, nor with common propylene bromide, $CH_3.CHBr.CH_2Br$, nor with monobromethylene, nor with either *alpha* or *beta* monobrompropylene, nor with $CHBr:C(CH_3)_2$. In failure of addition other reactions take place, the products of which have been determined. Evidently the affinities of these

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[1] N. Menschutkin and M. Vasileff, St. Petersburg, April, 1890: *Ztschr. phys. Chem.*, 5, 589.

[2] Menschutkin, 1895: *Ber. d. chem. Ges.*, **28**, 1398.

[3] G. Bredig, 1894: *Ztschr. phys. Chem.*, **13**, 288.

[4] G. Kleine, 1894: Chem. Centrbl., I. 16, from Ztschr. Naturwissenschaften, **66**, 1-72.

other products are factors in the problem as to the limits of alkyl union with nitrogen in organic bases.

In the studies of these limits phenyl has received less attention.[1] Diphenylamine is a weak base. Triphenylamine is indifferent to acids, and refuses addition with alkyl iodides. Triphenyl phosphine is stated to have a little capacity to hold alkyl iodides in union. Coming under the definition of a tertiary alkyl, phenyl has base-forming capacity distinctly greater than that of tertiary butyl, the interactions of all the CH groups in the ring in some way reinforcing the carbon which links to nitrogen, destitute as this carbon is in respect to direct hydrogen union. In pyridine there appears an altogether different character, an indivisible tertiary base of strength, with special additive capabilities. With alkyl iodides it forms certain addition compounds beyond those obtained even with trimethylamine. In pyridine the carbon linked to nitrogen is wholly in CH groups, and we may infer that all of the five of these groups are in some sense directly united to the nitrogen, though brought within a valence of three. Possibly also, the unsaturation of the unions of carbon to carbon, which is more active in pyridine than in benzene, imparts additive power to the nitrogen. The vigorous formation of pyridine methyl iodide was remarked by Anderson[2] shortly after his discovery of this base.

Mention of the addition compounds of pyridine with methyl iodide,[3] ethyl iodide,[4] propyl iodide and isopropyl iodide,[5] has been published in the accounts of various investigations devoted to other subjects, and therefore with partial examination and description of these particular products.[6] In resorting to pyridine as an analytical reagent for the identification of alkyls, Lip-

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[1] In setting out to build up secondary and tertiary amines in 1850, A. W. Hofmann formed ethylphenylamine, remarking that his "previous experimental researches suggested aniline for the foundation."—Phil. Trans., 1850, I., 97.

[2] Trans. Roy. Soc. Edinb., 21, (4) 571; *Ann. Chem.* (Liebig), 94, 360.

[3] O. Lange, On picolines by Ladenburg's transposition, 1885: *Ber. d. chem. Ges.*, 18, 3436.

[4] O. de Coninck, Analytical distinction between pyridine and quinoline, 1883: *Bull. Soc. chim.* [2], 40, 276.

[5] Ladenburg and Schraeder, On formation of propyl pyridines, 1884: *Ber. d. chem. Ges.*, 17, 1121, and further in other papers.

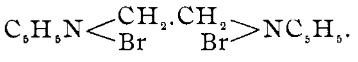
[6] A description of these four quaternary base iodides is given in another paper from this laboratory by A. B. Prescott.

pert[1] has recently reviewed the literature upon pyridine alkyl iodides, and has also contributed an account of the preparation, and certain of the properties of the obtainable butyl iodides of pyridine, namely, those of normal butyl, isobutyl, and secondary butyl. Tertiary butyl iodide did not form a permanent addition product with pyridine, in Lippert's hands, the reaction for its production yielding indications of pyridine hydriodide and of isobutylene. These transformation products are the same that have been obtained upon attempting to introduce tertiary butyl into aliphatic amines, and at all events have prevented the linking of more than one tertiary butyl group to the nitrogen of these amines.

It appears, therefore, that for secondary and tertiary alkyl halides, the limits of pyridine addition go beyond the limits of trimethylamine or triethylamine addition, while the former limits are parallel to the latter. On the other hand it is easier to form a primary amine or ammonium salt of a tertiary alkyl than it is to form a pyridinium salt of the same alkyl. Comparing pyridine addition with aliphatic base formation, we may apply the conclusions drawn by Menschutkin from comparisons among certain aliphatic bases themselves, that the capacity of the nitrogen atom in a base to exercise five units of valence, depends largely, he says, on the nature of the elements or groups to which the nitrogen is already united.

DIHALOGEN SUBSTITUTED HYDROCARBONS IN ADDITIVE REACTION WITH PYRIDINE.

The action of halides of "diatomic radicals" upon the tertiary amines was studied by Hofmann in London.[2] Pyridine ethylene bromide was obtained[3] in his laboratory a short time before he returned to Germany. This product was stable, and upon analysis was found to have the proportions of $(C_5H_5N)_2C_2H_4Br_2$. We may now express this composition by the formula



$$\mathrm{C_5H_5N}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{Br}\qquad\mathrm{Br}\end{matrix}>\mathrm{NC_5H_5}.$$

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[1] W. Lippert, On the decomposition of ethers by hydrogen halides, 1893: *Ann. Chem.* (Liebig), **276**, 181.

[2] Phil. Trans. Action of ethylene bromide upon trimethylamine, May 2, 1858, upon triethyl phosphine, June 25, 1860. Further, Proc. Roy. Soc., **9**, 293.

[3] Davidson, May 24, 1861: Proc. Roy. Soc., **11**, 261; *J. Chem. Soc.*, **14**, 161.

The next homologue in diprimary dibromine substitution is trimethylene bromide, $CH_2Br.CH_2.CH_2Br$, and we have obtained its addition compound with pyridine as follows: Pyridine of a boiling-point of 116°–118° C., and trimethylene bromide of a boiling-point of 165° C., were added together in the proportion of two molecules of the pyridine to one molecule of the bromide, and to the mixture one-fifth its volume of absolute alcohol was added. In Preparation I the mixture was heated in a sealed tube, at 105°–115° C. for four hours, when the product was a light brown crystalline mass, with a very little dark brown oily liquid and some gas escaping as the tube was opened. The crystals were drained, washed with alcohol, becoming of very light color, and recrystallized once from alcohol, becoming nearly white. Dried on a porous plate, the melting point of the crystals was 225°–226° C. In Preparation II the same materials, in same proportion, were digested in a sealed tube without applying heat, for a week. Crystallization began in clusters on the first day and increased steadily until apparently complete, this product being pure white. These crystals, without recrystallizing, were washed under suction with alcohol and dried on a porous plate in a vacuum desiccator. The melting point was the same as that of Preparation I.

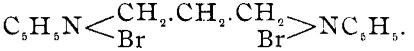
This compound is very soluble in water, less soluble in alcohol, and in ether, and but very slightly soluble in chloroform. It is slightly hygroscopic in the air. Kept in an open vessel for weeks it shows no indication of decomposition. At the high melting point there is gradual decomposition. Distilled at a little above its melting point, it yielded hydrobromic acid, and a very hygroscopic sublimate, which sublimed again unchanged, and had the properties of pyridine hydrobromide. No further work was done upon the decomposition products. Analysis of the addition product itself gave figures as follows:

	Calculated for $(C_5H_5N)_2C_3H_6Br_2$.	Preparation I. (1)	(2)	Preparation II.
Bromine ·······	44.43	44.11	44.07	44.42
Nitrogen ·······	7.78	8.08	8.46	7.84

A determination of the molecular weight was made with Preparation I by the cryoscopic method, using phenol as the solvent. Previous trial was made with acetic acid, the results of which indicated decomposition of the addition product. Had time permitted making the determination with the purer product in Preparation II, obtained later, results closer to the calculated molecular weight than could have been expected. The figures obtained with Preparation I were as follows, in which $M =$ molecular weight; $K =$ constant, which for phenol is 76; $g =$ grams of substance; $G =$ grams of solvent, and $\Delta =$ depression. These are taken in the formula $M = 100.K.\frac{g}{\Delta G}$.

No.	g.	G.	Δ	M.
1	0.4055	15.5	0.573°	346.8
2	0.6898	15.5	1.083°	312.0
3	0.2339	16.6	0.328°	328.0
4	0.3386	15.7	0.492°	332.8
5	0.3852	24.8	0.340°	347.1
6	0.6914	24.8	0.651°	326.0
$(C_5H_5N)_2C_3H_6Br_2$				359.15

The formula, therefore, appears to be



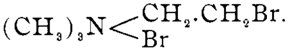
$$C_5H_5N\left<\begin{matrix}CH_2.CH_2.CH_2\\ Br\qquad\qquad\quad Br\end{matrix}\right>NC_5H_5.$$

This determination supports the formula adopted for the pyridine ethylenebromide of Davidson, as a dipyridine compound. Hofmann[1] found the trimethylamine ethylenebromide to have the proportions of a monammonium compound, $(CH_3)_3N.C_2H_4Br_2$, while, singularly enough, Kleine gives[2] the proportions in trimethylamine trimethylenebromide to be those of a diammonium compound $\Big((CH_3)_3N\Big)_2.C_3H_6Br_2$.

The composition of these four related dihalogen addition products, the aliphatic base and the aromatic base combinations respectively with substituted ethane and propane, may be compared as follows:

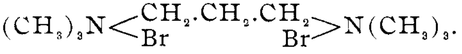
With trimethylamine:

The ethane derivative,



$$(CH_3)_3N\left<\begin{matrix}CH_2.CH_2Br.\\ Br\qquad\qquad\end{matrix}\right.$$

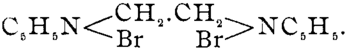
The propane derivative,



$$(CH_3)_3N\left<\begin{matrix}CH_2.CH_2.CH_2\\ Br\qquad\qquad\quad Br\end{matrix}\right>N(CH_3)_3.$$

With pyridine:

The ethane derivative,



$$C_5H_5N\left<\begin{matrix}CH_2.CH_2\\ Br\qquad Br\end{matrix}\right>NC_5H_5.$$

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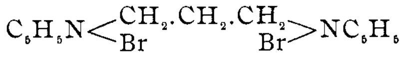
[1] 1858: Proc. Roy. Soc., 9, 293. "Addition of nitrate of silver precipitates only one-half of the bromine as bromide of silver, while even by protracted ebullition the second half remained untouched."

[2] Chem. Centrbl., 1894, I., 16.

The propane derivative, 

$$C_5H_5N\left\langle\begin{matrix}CH_2\\Br\end{matrix}\right..CH_2.\left.\begin{matrix}CH_2\\Br\end{matrix}\right\rangle NC_5H_5$$

As these results now stand, it appears, *first*, that pyridine is more reactive for addition with diprimary halogen groups than is trimethylamine ; *second*, that with the weaker base the one primary halogen group protects the other from addition when both these groups link together, not when they are separated by a CH_2 group. In this relation it may be noted as a conclusion of Bredig,[1] that in metameric diamines, the bases are stronger, the further removed are the amido groups.

We have studied the reaction of pyridine upon a few primary-secondary dihalogen substituted hydrocarbons, and have not obtained addition in any of these cases. The conditions of addition were digestion in sealed tubes at 80° to 100° C. Propylene bromide, $CH_3.CHBr.CH_2Br$, was treated in several operations, both with di-pyridine proportions and with mono-pyridine proportions, with the result of various products, but without an addition product. Pyridine hydrobromide was at all events obtained. Again, with ethylidine chloride no addition was obtained. Other conditions, however, will be brought to bear upon this class of pyridine additions, in work now in hand in this laboratory.

ANN ARBOR, MICHIGAN.

A PROPOSED SCHEDULE OF ALLOWABLE DIFFERENCE AND OF PROBABLE LIMITS OF ACCURACY IN QUANTITATIVE ANAYSES OF METALLURGICAL MATERIALS.[2]

BY E. D. CAMPBELL.

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WITHIN the past twenty years, metallurgical practice has grown to depend more and more upon a chemical knowledge of the material employed in the various operations. On account of this dependence it has become necessary to have accurate as well as rapid methods for the determination of the elements which take an active part in the different processes.

Many methods for the determination of the various elements

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[1] *Loc. cit.*

[2] Read before the Chemical Section of the American Association for the Advancement of Science, Sept. 2, 1895.