can be only partially oxidized by a ferro–ferricyanide oxidation–reduction buffer (20:1) under conditions which permit complete oxidation of II. (d) The cathodic mobility of I on ionophoresis in 1% ammonium acetate on Whatman no. 5 paper is less than that of II by at least one order of magnitude.

Preparations of I, as obtained by the Keilin–Hartree procedure, usually exhibit a purity of 10–50%, based on spectral absorption properties and the assumption that the extinction coefficients at the characteristic absorption maxima are closely similar to those for II. Electrophoretic treatment of such preparations results in a 2- or 3-fold purification because of removal of colorless impurities which migrate rapidly toward the cathode.

The conclusion that I is not identical with II is further strengthened by the observation that I can be oxidized via mammalian cytochrome oxidase, if some II is added to the reaction mixture (see Fig. 1). Complete oxidation in this manner cannot be attained, indicating in agreement with (c) above, that the oxidative–reduction potential of I is slightly positive with respect to II.

It is tempting, but premature, to discuss the many intriguing possibilities raised by the presence of this new cytochrome in photosynthetic organisms. We may note, however, that the existence of the bacterial cytochrome may provide the basis for a mechanism of photochemical H-transport and an explanation for the absence of a light-stimulated respiration in the photoheterotrophes. It is suggested that I be called tentatively "cytochrome-c2".[3] Further researches on the properties of this and other haem-proteins in the photosynthetic bacteria are proceeding.

The investigations at Washington University have been made possible by grants from the C. F. Kettering Foundation and the U. S. Public Health Service. We are indebted to Dr. S. Velick, Dept. of Biochemistry, Washington University Medical School, for aid in the experiments on electrophoretic purification of the bacterial cytochrome.

(3) R. Hill and D. Keilin, private communication.

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RECEIVED DECEMBER 3, 1953

BEHAVIOR OF AN ION-EXCHANGE RESIN IN LIQUID AMMONIA

Sir:

In the course of a study of ion species present in liquid ammonia solution, use has been made of the cation exchange resin Dowex-50.[1] The ammonium form of the resin, dried 16 hours *in vacuo*, was washed copiously at −33° by repeatedly condensing fresh anhydrous ammonia upon it and then filtering. The resin was exposed, in a column operation, to a solution of liquid ammonia which contained the products of the reaction of potassium with monoammino boron trifluoride[2,3] (0.1901 g. K, 0.4380 g. $BF_3 \cdot NH_3$).

The total product from the 0.6281 g. of reactants dissolved in about 35 ml. of ammonia, was passed through a resin column, one cm.^{2} × 12 cm. at a rate that varied between 1 and 2 ml. per minute. The resin, which was largely in the ammonium form, quantitatively removed potassium from the solution. Boron and fluorine passed through the resin bed. The eluate solution was evaporated to dryness and the solid residue, which weighed 0.4457 g. after evacuation, was shown to be mainly $BF_3 \cdot NH_2$ by X-ray diffraction analysis.[4]

After the resin column had been washed until the washings gave negative tests for boron, a solution of ammonium chloride was passed through the column. The 11.7 g. of resin had a calculated capacity of 58.5 meq. cation, 10.9 meq. of potassium being on the resin after two exchange experiments. The passage of a total of 134 meq. ammonium ion (in approx. 1.5 *M* NH_4Cl solution) through the column resulted in the elution of only 0.4 meq. potassium.

The behavior of Dowex-50 in liquid ammonia parallels its behavior in water. A solution of ammonium chloride in ammonia behaves like a solution of hydrogen chloride in water: neither are efficient in stripping the resin of potassium ions. Potassium ion efficiently displaces ammonium ion from the resin in ammonia just as it displaces hydronium ion from the resin in water solution.

It appears that ion-exchange techniques of separations, purifications, and syntheses can be used successfully in the liquid ammonia medium.

(1) These studies were inspired by a paper which described the use of a cation exchange column in the study of KBF_3OH: see C. A. Wamser, THIS JOURNAL, **73**, 419 (1951).

(2) In a forthcoming publication it will be shown that $BF_3 \cdot NH_3$ reacts with *only one* equivalent of potassium in dilute ammonia solutions. When the resulting solution is evaporated to dryness and analyzed by X-ray diffraction the pattern of KF is found. Quantitative recovery of the total solid products and analysis of the gaseous and solid products support the following interpretation:

$$K + BF_3 \cdot NH_3 \longrightarrow KF + BF_2NH_2 + 1/2\ H_2$$

This equation accounts for all our observations, but it is emphasized that we have not as yet isolated the boron compound.

(3) For a description of the reaction of sodium with $BF_3 \cdot NH_3$ in liquid in ammonia see C. A. Kraus and E. H. Brown, *ibid.*, **51**, 2690 (1929).

(4) The X-ray powder diffraction of $BF_3 \cdot NH_3$ as obtained in this laboratory does not check with that reported by A. W. Laubengayer and G. F. Condike, *ibid.*, **70**, 2274 (1948). As prepared here in two ways, or as recrystallized from either water or liquid ammonia, the compound yields the following lines:

4.87 (m) 4.01 (s) 3.65 (s) 3.37 (s) 2.87 (m) 2.72 (s)
2.45 (m) 2.34 (m) 2.24 (s) 1.97 (w) 1.81 (m) 1.65 (w)

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RECEIVED NOVEMBER 20, 1953

THE STRUCTURE OF PITHECOLOBINE

Sir:

Some time ago we described an alkaloid from the bark of *Pithecolobium saman* (Benth.)[1] $C_{22}H_{46}N_4O_2$ (one amide group, one hydroxy group, one ring, no double bond) which on reduction with $LiAlH_4$ gave desoxypithecolobine $C_{22}H_{48}N_4$ (one ring, no double bond). Analytical difficulties with even highly

(1) K. Wiesner, D. M. MacDonald, Z. Valenta and R. Armstrong, *Can. J. Chem.*, **30**, 761–772 (1952).

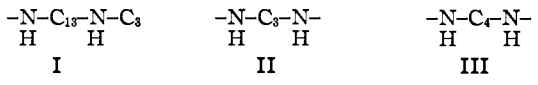
purified samples make it impossible to distinguish these formulas from those containing one more CH_2. We have now identified all the carbons as recognizable fragments and established thereby the C_{23} formula. Desoxypithecolobine contains four secondary nitrogens, as by acetylation it gave a glassy *neutral* tetraacetyl derivative which by Li-AlH_4 reduction gave tetraethyldesoxypithecolobine, characterized by a homogeneous countercurrent distribution peak and distillation of the peak fractions (b.p. 211–212°, collar flask 0.05 mm.; found: C, 75.05; H, 13.22; N, 11.60). In this latter compound all nitrogens are tertiary as there is no N–H peak in the infrared and the compound is recovered unchanged from acetylation (identity of infrared spectrum).

Hofmann degradation of methylated desoxypithecolobine gave[1] in the first stage tetramethyl-1,4-*tetra*methylenediamine and a mixture of bases. The second stage performed on these bases gave a diene $C_{13}H_{24}$ (b.p. 107–112°, collar flask 12 mm., U.V. $\lambda_{max.}$ 227 mμ, log ϵ = 4.38; found: C, 86.55; H, 13.26; uptake of hydrogen, 2 moles). Measurements of boiling point and molecular weight performed on the tetrahydro product distinctly favor the C_{13} formula. There was further isolated[1] from the mixture of bases a mixture of N_1 bases analyzing quite well for $C_{17}H_{33}N$. These took up 2 moles of hydrogen on hydrogenation and on subsequent Hofmann degradation gave a hydrocarbon $C_{13}H_{26}$ and dimethyl-*n*-propylamine identified by mixed melting point and infrared spectrum of the picrate and analysis. The $C_{13}H_{26}$ hydrocarbon took up one mole of hydrogen and gave a hydrocarbon $C_{13}H_{28}$ (found: C, 84.77; H, 15.09; b.p. 129–132°, collar flask 40 mm.). This leaves only 3 carbons to be identified. These in view of the low N-CH_3 values obtained on desoxypithecolobine (found: (N)CH_3, 3.11) must form one fragment.

Hofmann degradation of methylated pithecolobine gave in the first stage a large neutral fraction which was hydrogenated, after which the individual compounds were separated by chromatography. In addition, tetramethyl-1,3-*tri*methylenediamine was identified in good yield by mixed melting point, analysis, and infrared spectrum of the picrate. From the hydrogenated neutral substances a compound $C_{13}H_{27}ON$ (m.p. 88–90°, found: C, 73.14; H, 12.72; N, 6.66) has been isolated which has all the characteristic infrared bands of a saturated primary amide. Further, a compound $C_{16}H_{33}ON$ (m.p. 49–50°, found: C, 75.14; H, 13.00; N, 5.52) with all the characteristic infrared bands of a saturated secondary amide was obtained. This on hydrolysis gave *n*-propylamine identified by infrared spectrum of the hydrochloride. As two C_3 fragments have now been obtained which must have a different origin, 23 carbons have thus been accounted for.

Chromatography of the neutral substances before hydrogenation gave a small yield of a monounsaturated primary amide $C_{13}H_{25}ON$ (m.p. 67–69°, found: C, 73.88; 12.02; N, 6.81). An oily secondary amide was obtained which on acid hydrolysis slowly liberated propionic aldehyde identified by paper chromatography and ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone. This may be explained by an isomerization and hydrolysis of an allylamide.

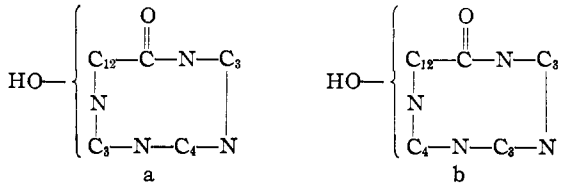
Keeping in mind the secondary nature of all nitrogens in desoxypithecolobine the presence of



I II III

has been demonstrated.

The evidence thus points to structure (a) or (b)



a b

for pithecolobine and the corresponding structures, with the amide and hydroxy group reduced, for desoxypithecolobine. On the basis of indirect suggestive evidence to be published later, we favor (a) for the arrangement of fragments.

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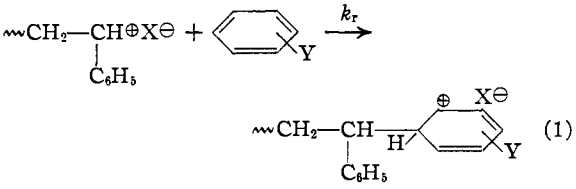
RECEIVED NOVEMBER 10, 1953

IONIC POLYMERIZATION. A METHOD FOR MEASURING THE RELATIVE RATES OF ATTACK OF A CARBONIUM ION PAIR ON AROMATIC COMPOUNDS IN HOMOGENEOUS SOLUTION. NUCLEOPHILICITY FACTORS

Sir:

We have been able to utilize the useful chain transfer equation developed for free radical polymerization[1] as a sensitive method for measuring quantitatively the relative rates of attack of a carbonium ion pair on aromatic compounds in homogeneous solution. *With this treatment it is possible to assign a relative numerical factor, here called a nucleophilicity factor, for attack of such an ion pair on an aromatic nucleus*



(1)

It is of primary interest and importance that the Mayo equation (2) is applicable to substances which retard the rate of cationic catalyzed polymerization. This is not the case for free radical polymerization due to the occurrence of termination involving two radicals, which leads to dependence of the degree of polymerization on the radical concentration. Thus a typical $1/\bar{P}_n$ *vs.* [S]/[M] plot will not be linear for a retarder in a radical system. In a cationic chain process, however, it is reasonable to assume that termination involving two ion pairs does not occur, and the degree of polymerization should be independent of the concentration of ion pairs.

(1) F. R. Mayo, THIS JOURNAL, 65, 2324 (1943).