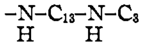
purified samples make it impossible to distinguish these formulas from those containing one more CH_2. We have now identified all the carbons as recognizable fragments and established thereby the C_{23} formula. Desoxypithecolobine contains four secondary nitrogens, as by acetylation it gave a glassy *neutral* tetraacetyl derivative which by $LiAlH_4$ 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.

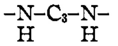
Chromatography of the neutral substances before hydrogenation gave a small yield of a monounsaturated primary amide $C_{13}H_{25}ON$ (m.p. 67–69°, found: C, 73.88; 12.02; N, 6.81). An oily secondary amide was obtained which on acid hydrolysis slowly liberated propionic aldehyde identified by paper chromatography 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



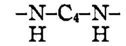
$$\underset{H}{-N}-C_{13}-\underset{H}{N}-C_3$$

I



$$\underset{H}{-N}-C_3-\underset{H}{N}-$$

II

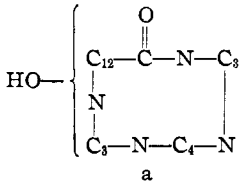


$$\underset{H}{-N}-C_4-\underset{H}{N}-$$

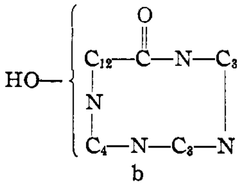
III

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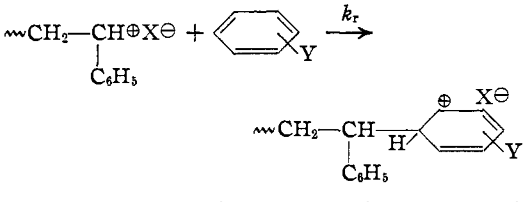
IONIC POLYMERIZATION. A METHOD FOR MEASURING THE RELATIVE RATES OF ATTACK OF A CARBONIUM ION PAIR ON AROMATIC COMPOUNDS IN HOMOGENEOUS SOLUTION. NUCLEOPHILICITY FACTORS

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.

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(1) F. R. Mayo, This Journal, 65, 2324 (1943).

Retardation and chain transfer were studied in the polymerization of styrene by stannic chloride catalyst in carbon tetrachloride–nitrobenzene solvent mixture. The data were correlated by means of the aforementioned equation which may be written as

$$\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_{no}} = \frac{k_r}{k_p}\frac{[R]}{[M]} \qquad (2)$$

$[R]/[M]$ represents the mole ratio of retarder or chain transfer agent (R) to monomer, k_r/k_p the ratio of the rate constant for reaction of ion pair with R to the propagation rate constant, and the terms $\bar{P}_n$ and $\bar{P}_{no}$ the number average degree of polymerization in the presence and absence of R, respectively.

For each compound reported in Table I polymerizations were carried out at about six different concentrations of R, and at least two control polymerizations containing no R were carried out at the same time. The concentrations of monomer, catalyst and nitrobenzene were the same in all runs, and the total volume per cent. of carbon tetrachloride plus R was also maintained constant.[2]

Polymerizations were ordinarily stopped at 10–15% conversion by precipitation of the polymer in methanol. The degrees of polymerization were determined from measurements of intrinsic viscosities in benzene solution at 30°, using the intrinsic viscosity–molecular weight relation of Pepper[3] for unfractionated polystyrene. $\bar{P}_{no}$ is about 200 under the conditions of our experiments, and the concentrations of R were chosen over a range so that at the highest concentration $\bar{P}_n$ was about one-third to one-half of $\bar{P}_{no}$.

In each case a plot of $1/\bar{P}_n - 1/\bar{P}_{no}$ *vs.* $[R]/[M]$ is linear and passes through the origin. The values of k_r/k_p obtained from the slopes of these plots are listed in Table I, together with relative values of k_r. These values are consistent with the mechanism proposed (1), based on qualitative knowledge of the Friedel–Crafts reaction.

TABLE I

POLYMERIZATION DATA[a]

Compound (R)	k_r/k_p	k_r (relative) neucleophilicity factor[b]
p-Cymene	0.0044	0.42
p-*t*-Butyltoluene	0.0062	0.69
p-Chloroanisole	0.0082	0.78
p-Xylene	0.0105	1
Thiophene	0.98	93
Anisole	1.62	154

[a] Initial monomer concentration = 1.95 *M;* stannic chloride concentration = 0.023 *M;* temperature 0°. [b] The value of k_p is assumed to be identical in all cases; a value of k_r = 1 is arbitrarily assigned to *p*-xylene.

Relative rates of polymerization were measured in the absence and presence of additional compounds, using a precipitation technique. Over the measured range, about 10–80% conversion, under the conditions employed here the reaction is pseudo first order with respect to monomer.

The hydrocarbons have little or no effect on the rate, indicating that only chain transfer is occurring with these compounds. However, thiophene retards the rate strongly and anisole relatively weakly.

This method provides a sensitive means of studying the effect of different alkyl groups in mono- and higher substituted alkyl benzenes on the reactivity toward an ion pair of the general type involved in the Friedel–Crafts reaction. Where possible, such results could be compared with published data concerning complex formation with electrophilic species[4,5,6] and relative rates of halogenation.[7,8]

Other related problems are under investigation using this general experimental procedure.

We gratefully acknowledge the generous support of the Office of Naval Research.

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[2] This was done in order to keep the dielectric of the medium approximately constant, since the aromatic hydrocarbons in the table all have dielectric constants close to that of carbon tetrachloride. In the case of *p*-chloroanisole, this procedure may have permitted a significant variation in solvent dielectric; for anisole and thiophene the concentrations employed were small (<0.025 *M*) and the dielectric was probably not appreciably affected.

[3] D. C. Pepper, *J. Polymer Sci.*, **7**, 347 (1951).

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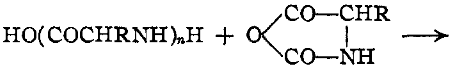
THE MECHANISM OF POLYMERIZATION OF N-CARBOXY-α-AMINO ACID ANHYDRIDES

Sir:

The polymerization of N-carboxy-α-amino acid anhydrides (I) is believed to proceed according to reaction (1).[1,2] It was assumed, by analogy with



I

$$\mathrm{HO(COCHRNH)_nH} + \mathrm{O}\!\left\langle\begin{matrix}\mathrm{CO{-}CHR}\\ \mathrm{CO{-}NH}\end{matrix}\right. \longrightarrow \mathrm{HO(COCHRNH)_nCOCHRNH_2} + \mathrm{CO_2} \qquad (1)$$

the polymerization of ethylene oxide, that no termination reaction occurs, and that propagation proceeds by the addition of I to the terminal free amino group present in each polypeptide chain. Water-initiated polymerizations should therefore lead to polypeptides with equal numbers of amino and carboxyl terminal groups, while amine-initiated polymers should contain amino, but no carboxyl terminal groups. Furthermore, it should be possible to prepare poly-α-amino acids of very high molecular weight.

The fact that the N-carbonyl group of I reacts to a certain extent with sodium methoxide,[3] suggested to us that reaction (2), which constitutes a *termination* reaction, should also occur. Termina-

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(2) L. Gold, *J. Chem. Phys.*, **21**, 1190 (1953).

(3) A. Berger, M. Sela and E. Katchalski, *Anal. Chem.*, **25**, 1154 (1953).