diameter of 0.002 Å., which is probably reasonable for the experimental error in most cases.

The straight lines in the accompanying figure have the theoretical slopes, that is, the B_{CX} value of Table I. The intercepts, as mentioned above, are arbitrary. The scales of the three graphs are the same, so that the relative slopes may readily be observed also. The calculated and observed slopes are all approximately the same for each series of halogens, and the relative slopes for the different series are predicted correctly.

The particular molecules included in this study are chosen simply because they are the ones for which accurate bond-length data are available. One other series might be considered: C–H bonds. Here, however, it is found that there is so much variation in the experimental values, due to difficulties encountered in averaging the results for the deuterium isotopes studied, and the results are so sensitive to the methods employed,[8] that it proves impossible to distinguish bond length variations from experimental error and ambiguity for C–H bonds.

We emphasize that, in calculating our theoretical slopes, no "adjustable parameters" have been employed; the constants involved are all carried over directly from the theory of reference (2), which in turn uses only accepted polarizabilities, screening constants, and covalent radii. Hence the results are believed to lend some support both to the theory outlined here and to the theory of reference (2).

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Polyphosphoric Acid as a Reagent in Organic Chemistry. IV. Conversion of Aromatic Acids and their Derivatives to Amines[1]

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RECEIVED DECEMBER 8, 1952

In a continuation of investigations of the use of polyphosphoric acid as a reagent in organic reactions[2,3] it has been found that aromatic acids can be converted to aryl amines by treatment with hydroxylamine and commercial polyphosphoric acid.[4] The reaction is carried out by heating a mixture of the reactants, with stirring, until rapid evolution of carbon dioxide begins, usually in the range of 150–170°. At such temperatures the reaction normally is complete in five to ten minutes, and the mixture is poured over crushed ice to give an aqueous solution of the amine phosphate.

The yields of crude products obtained from various acids are reported in Table I. In general, acids containing electron-donating substituents were found to give higher yields than those containing electron-withdrawing groups. This is in agreement with the results obtained by Hauser[5] in his studies on the effect of substituents on the Lossen rearrangement. Acids which gave poor yields of amines produced large amounts of dark colored, acid-insoluble material of very indefinite melting point. The two aliphatic acids studied, valeric acid and caprylic acid, failed to yield more than mere traces of the expected amines. Caprylohydroxamic acid likewise failed to yield *n*-heptylamine when subjected to similar conditions.

Many acid derivatives also underwent the reaction (see Table I). However, with the exception of esters, the yields were generally lower than with the corresponding acids themselves. *p*-Chlorobenzamide, N-methyl-*p*-chlorobenzamide and N-methylbenzamide yielded no *p*-chloroaniline or other identifiable product. The reason for this unexpected discrepancy is not known. It is interesting to note that some ketones may be transformed into the corresponding amines by treatment with two moles of hydroxylamine. The first step involves a Beckmann rearrangement[3] to the substituted amide while the second step involves cleavage of this acid derivative to give two moles of amine.

The exact course of the reaction has not been elucidated but it seems likely that a hydroxamic acid is an intermediate. Indeed, hydroxamic acids themselves are smoothly converted to amines in hot polyphosphoric acid. Potassium benzohydroxamate and potassium α-naphthohydroxamate yielded aniline (67%) and α-naphthylamine (73%), respectively. The transformation of *o*-phenylbenzoic acid into phenanthridone and that of salicylic acid into benzoxazolone can be explained by assuming an isocyanate to be an intermediate. Thus it seems likely that the process is a variant of the Lossen reaction.

For most of the reactions the sulfate and hydrochloride of hydroxylamine could be used interchangeably with but little influence on the course of the reaction. However, there were three notable exceptions; hydroxylamine hydrochloride gave markedly better yields with salicylic acid and with benzophenone, but hydroxylamine sulfate was required with *p*,*p*'-dichlorobenzophenone.

Although the method appears to be less generally applicable than the Curtius and Hofmann conversions of acids to amines, it is very attractive within its field of application. Only the simplest apparatus is required and the total reaction time is ten minutes or less. It is more conveniently carried out than the Schmidt reaction, which must be conducted with due regard to the properties of hydrazoic acid.

Experimental

General Method.—To 25–50 g. of polyphosphoric acid was added 5 g. of the carboxylic acid and slightly more than the theoretical amount of hydroxylamine sulfate or hydrochloride. The mixture was stirred mechanically and heated slowly on an oil-bath. When the chloride salt was used hydrogen chloride was evolved from the reaction mixture as the temperature approached 100°. Upon further increase in temperature the reactants gradually entered solution. In the range 150–170° there was a rapid evolution of carbon dioxide and the mixture darkened considerably. When the frothing had ceased the mixture was poured onto crushed ice. The insoluble material was removed and the filtrate was neutralized with potassium hydroxide. The liberated amine, if liquid, was extracted with several portions of benzene. The combined extracts were dried over sodium hydroxide pellets and then treated with dry hydrogen chloride gas. The precipitated hydrochloride was collected and dried in a desiccator. If the amine was solid

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(1) Presented in part at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September 17, 1952.

(2) H. R. Snyder and R. W. Roeske, THIS JOURNAL, **74**, 5820 (1952).

(3) E. C. Horning, V. L. Stromberg and H. A. Lloyd, *ibid.*, **74**, 5153 (1952).

(4) The authors are indebted to Dr. Howard Adler, Victor Chemical Works, Chicago, Ill., for generous supplies of polyphosphoric acid.

(5) C. R. Hauser and collaborators, THIS JOURNAL, **59**, 121, 2308 (1937); **61**, 618 (1939).

TABLE I

Reactant	Isolated or expected product	Yield, %	M.p., °C.	Reported m.p., °C.
β-Naphthoic acid	*β*-Naphthylamine	82	107–109	111–112
α-Naphthoic acid	*α*-Naphthylamine	80	43–45	50
Benzoic acid	Aniline hydrochloride	66	190–192	198
m-Toluic acid	*m*-Toluidine hydrochloride	76	223–225	228
p-Toluic acid	*p*-Toluidine hydrochloride	72	238–239	243
o-Bromobenzoic acid	*o*-Bromoaniline hydrochloride	53[a]		
m-Bromobenzoic acid	*m*-Bromoaniline hydrochloride	46[a]		
p-Bromobenzoic acid	*p*-Bromoaniline hydrochloride	43[a]		
p-Chlorobenzoic acid	*p*-Chloroaniline	32	69–70	70–71
Salicylic acid	Benzoxazolone	33[b]	137–138	138
o-Phenylbenzoic acid	Phenanthridone	40	292	293
m-Nitrobenzoic acid	*m*-Nitroaniline	53	109–110	112
o-Nitrobenzoic acid	*o*-Nitroaniline	0		
p-Nitrobenzoic acid	*p*-Nitroaniline	0		
Valeric acid	*n*-Butylamine	0		
Caprylic acid	*n*-Heptylamine	0		
Ethyl benzoate	Aniline hydrochloride	68	190–193	198
Benzamide	Aniline hydrochloride	43	190-193	198
Benzoyl chloride	Aniline hydrochloride	51	189–192	198
Benzonitrile	Aniline hydrochloride	20	190–192	198
p-Chlorobenzamide	*p*-Chloroaniline	0		
Benzanilide	Aniline hydrochloride	76	188–191	198
p,p'-Dichlorobenzanilide	*p*-Chloroaniline	48	66–70	70–71
p,p'-Dichlorobenzophenone oxime	*p*-Chloroaniline	40	65–68	70–71
p,p'-Dichlorobenzophenone	*p*-Chloroaniline	15	69–70	70–71
Benzophenone	Aniline hydrochloride	66	188–191	198
N-Methyl-*p*-chlorobenzamide	*p*-Chloroaniline, methylamine	0		
N-Methylbenzamide	Aniline, methylamine	0		

[a] Identity confirmed by conversion to acetyl derivative. [b] Recrystallized once from water.

it was filtered from the basic solution directly and then dried. The yields of crude amines or amine hydrochlorides obtained in this way are reported in Table I.

β-Naphthylamine.—To a mixture of 1.7 g. (0.24 mole) of hydroxylamine hydrochloride and 4.0 g. (0.23 mole) of *β*-naphthoic acid was added 50 g. of polyphosphoric acid. The mixture was stirred mechanically and the temperature was gradually raised. At 160° the evolution of carbon dioxide had ceased and the brown mixture was poured over 250 g. of crushed ice. Filtration of the resulting mixture yielded 0.7 g. of an orange colored solid, which displayed no definite melting point. The filtrate was neutralized with potassium hydroxide and the precipitated amine was collected and dried. The yield was 2.7 g. (82%) of light tan *α*-naphthylamine, m.p. 107–109° (lit. 111–112°).

Aniline from Benzophenone.—To a mixture of 2.1 g. (0.030 mole) of hydroxylamine hydrochloride dissolved in 20 g. of polyphosphoric acid was added 1.82 g. (0.010 mole) of benzophenone. The mixture was heated with constant stirring to 160–165° for ten minutes. The purple mixture was poured over 100 g. of crushed ice and the small amount of insoluble material was removed by filtration. The filtrate was made strongly basic with potassium hydroxide and then extracted thoroughly with benzene. The extracts were dried over sodium hydroxide and then saturated with dry hydrogen chloride. The precipitated aniline hydrochloride was collected and dried in a desiccator. The dry hydrochloride had a light purple tinge and melted at 188–191°. The yield was 1.72 g. (66%).

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Predicted Isotopic Enrichment Effects in Some Isotopic Exchange Equilibria Involving Carbon-14

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RECEIVED NOVEMBER 28, 1952

The equilibrium constants of a considerable number of isotopic exchange reactions have been predicted by the methods of statistical thermodynamics.[1,2] No data of this type have been reported in regard to carbon-14/carbon-12 exchanges. Concurrently with a recent experimental study of such an exchange,[3] it was found desirable to make a number of predictions of this nature. This note presents a brief summary of the results of these and of some additional computations, in the belief that they may prove of interest to others investigating carbon-14 isotope effects.

The procedure was as given by Urey,[1] utilizing the spectroscopic data referred to in the tabulation below. The vibrations for the corresponding carbon-14-containing compounds were determined by use of the harmonic oscillator approximation for diatomic molecules,[4] and of normal vibration equations (usually the valence-force-field approximation) for polyatomic molecules.[5] In certain indicated instances, earlier frequency assignments were checked or modified on the basis of the vibration equation treatment. The partition function ratios Q_{14}/Q_{12} at the three temperatures 273.16, 293.16 and 313.16°K., respectively, are given for each of the eighteen compounds treated. The equilibrium constant of any probable exchange reaction between a pair of these compounds at any of the temperatures given is then readily predicted

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(3) D. R. Stranks and G. M. Harris, *J. Phys. Chem.*, **56**, 906 (1952).

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(5) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.