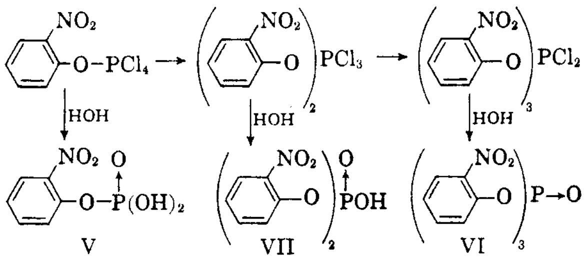

Di-ortho-substituted phenols. In view of the instability to moisture of the *ortho*-substituted phenols discussed above, it seemed that perhaps the more hindered 2,6-disubstituted phenols might form more stable compounds. One of the most hindered compounds of this type, 2,6-di-*tert*-butyl-*p*-cresol, was studied because of its ready availability.[13] However, even under vigorous reflux conditions in benzene or carbon tetrachloride, no reaction appeared to take place.

As further examples of di-*ortho*-substituted types, the reactions of 2,4,6-trihalophenols with phosphorus pentachloride were investigated. The trichlorophenol reacted at room temperature whereas the tribromo- and triiodophenols required heat. The products of these reactions appeared to be somewhat more stable to atmospheric moisture than the mono-*ortho*-substituted compounds previously investigated; however, the stability was not outstanding.

At the present time, in view of the more interesting results obtained in related work,[10] we do not contemplate any further work along the lines discussed in this paper.

EXPERIMENTAL

Reaction of phenols with phosphorus pentachlorides. The general procedure used in all of the reactions is described. In order to minimize polysubstitution of phosphorus pentachloride and to favor the formation of the monosubstituted compound, the reactions were run in such a way as to keep the concentration of the phenol at a minimum at all times, and to keep phosphorus pentachloride in excess during the reaction. This was done by adding the phenol dropwise to the phosphorus pentachloride.

A solution of 0.100 mole of the phenol dissolved in approximately[14] 50 ml. of purified ACS grade benzene was added dropwise by means of a dropping funnel to a stirred suspension of 0.100 mole of phosphorus pentachloride in approximately 50 ml. of benzene in a three-neck flask. The flask was equipped with a condenser which was attached to a calcium chloride drying tube which led in turn to a safety bottle and then to a solution of sodium hydroxide for absorption of hydrogen chloride. By the completion of the addition, the phosphorus pentachloride had reacted and gone into solution. The reaction mixture was allowed to stir for about 1-3 hr. after the completion of addition. The benzene solution was then transferred to a one-neck flask and the solvent removed *in vacuo* to obtain the crude product.

Since the present investigation was an exploratory study, no elaborate precautions were taken to exclude atmospheric moisture in the handling of the compounds. Thus, the results are of a qualitative nature. Since the compounds prepared were very hygroscopic—some liquefying almost immediately on contact with atmospheric moisture—the melting points and analyses are not reported because of the questionable purity of the compounds. In order to obtain pure compounds for reliable melting points and analyses, rigorous dry box techniques are recommended.

With the exception of the compound obtained from salicylaldehyde, which was an oily liquid, all of the other compounds were white solids.

Reaction of ortho-nitrophenol. The reaction was carried out according to the general procedure above. After standing for several days, a solid deposited from the benzene solution (before removal of solvent). The benzene solution was decanted and the solid collected, tris(*ortho*-nitrophenyl)-phosphate (VI) and weighed 2.0 g. after drying. The melting point, after recrystallization from purified isopropyl alcohol, was 126.4–128.0° (total immersion thermometer) (lit.[15] 126°). The benzene solution from the decantation, was evaporated *in vacuo* leaving a solid mass weighing 13.4 g. The solid was unstable to moisture. It was hydrolyzed by adding ice. A vigorous reaction took place with evolution of hydrogen chloride and formation of a brown oil which solidified on standing for about 2 hr. The solid was collected by filtration and washed with water. The wash water appeared to hydrolyze and dissolve the solid on the Büchner funnel, since after drying over calcium chloride only 1.2 g. of the solid remained. A comparison of the ultraviolet spectrum of the yellow filtrate with that of an aqueous solution of *ortho*-nitrophenol confirmed the presence of this compound in the filtrate. Thus it would appear that the solid which is probably the mono- and diphosphate esters, is readily hydrolyzed by water into *ortho*-nitrophenol and phosphoric acid. The molybdate test for phosphate showed its presence in the filtrate. The solid from the hydrolysis melted 164.5–166.0°. Attempts made to recrystallize the compound were unsuccessful since the compound was either too soluble or too insoluble in the many solvents tried. No combination of mixed solvents was found to be satisfactory. The compound decomposed into *ortho*-nitrophenol during an attempted sublimation under reduced pressure. Chromatography over silica gel was unsuccessful.

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(13) The authors express thanks to Shell Chemical Corp. and to Koppers Co., Inc. for samples of this compound.

(14) If necessary to dissolve the phenol completely, larger volumes of benzene were occasionally used.

(15) A. Engelhardt and P. Latschinow, *J. Russ. Phys. Chem. Soc.*, **2**, 116; *Z. für Chemie*, **1870**, 230; (*Beilsteins Handbuch der Organischen Chemie, Band*, **6**, vierte auflage, Verlag von Julius Springer, Berlin, 1923, p. 222) prepared this compound by heating *ortho*-nitrophenol and phosphorus pentachloride and treating the reaction product with water.

Infrared Spectra of Acid Azides[1]

EUGENE LIEBER[2] AND EDWIN OFTEDAHL

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Recent investigations[3,4] have demonstrated that reactions which theoretically should lead to thiocar-

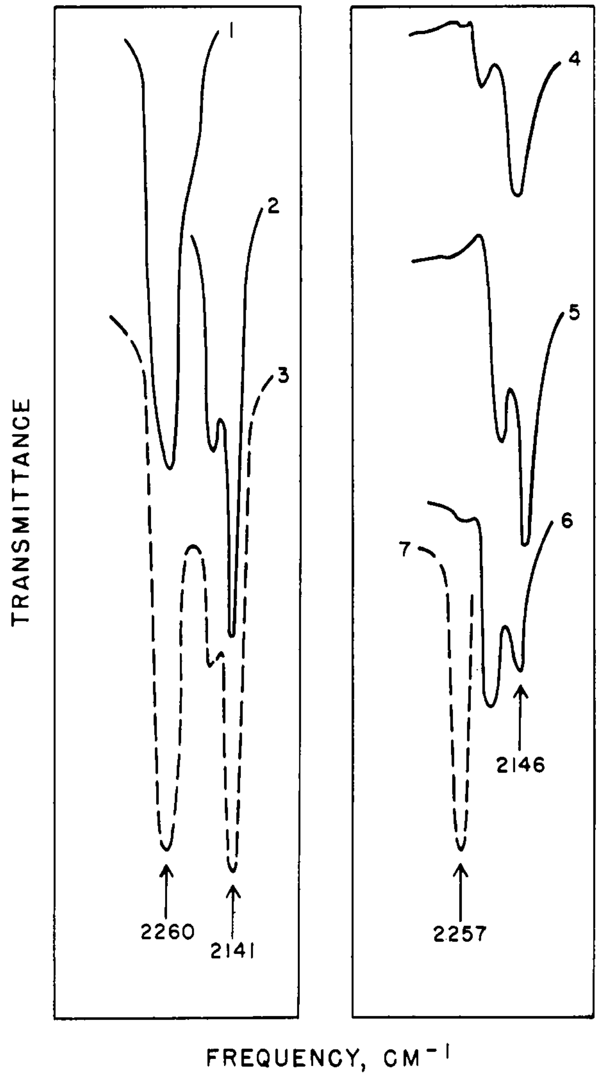
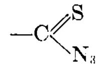
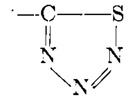


Fig. 1. (1) Phenylisocyanate by decomposition of benzazide. (2) Benzazide. (3) An equal mixture of phenylisocyanate and benzazide. (4) 3,5-Dinitrobenzazide. (5) *para*-Nitrobenzazide. (6) *meta*-Nitrobenzazide. (7) *meta*-Nitrophenylisocyanate by decomposition of *meta*-nitrobenzazide.

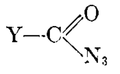
bamyl azides (I) are in reality derivatives of the thiatriazole ring system (II). Evidence for this observation was discovered simultaneously and independently by Scott,[3] Lieber,[4] Smith,[5a] and Jensen[5b] by infrared absorption spectroscopy, although chemical evidence is now available[4,5] to support this conclusion. On the other hand, chemical and spectroscopic evidence,[3,6] while limited, clearly demonstrates the azide structure of carbamyl azides (III).



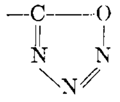
I



II



III. Y = N
IV. Y = alkyl or aryl



V

In reviewing the evidence for structure III, infrared absorption data were also sought for organic acid azides (IV). There has been no systematic study[7] on the infrared spectra of organic acid azides of structure IV, although this is not surprising since acid azides are explosives of varying degree of sensitivity[8] and are usually used as intermediates without isolation.[8b] Nevertheless, in spite of their sensitive nature, it was deemed of interest to examine the infrared absorption spectra of the more readily accessible and purifiable acid azides to determine the possibility of their existence as oxatriazoles (V) and/or possible group frequency shifts due to the proximity of the strong electron-withdrawing carbonyl group. This communication reports upon the preliminary results of this study. Table I and Figure 1 summarize the data obtained. All spectrum were obtained as mulls.

TABLE I

FREQUENCIES, CM.⁻¹

RN_3 R =	N_3 (Asym)		N_3 (Sym)	C=O
$C_6H_5C(O)$-	2179 (m)	2141 (s)	1238 (s)	1709 (s)
3-NO_2-$C_6H_4C(O)$-	2203 (s)	2146 (m)	1241 (m)	1701 (s)
4-NO_2-$C_6H_4C(O)$-	2193 (s)	2146 (s)	1233 (s)	1701 (s)
3,5-$(NO_2)_2$-$C_6H_3C(O)$-	2237 (m)	2155 (s)	1258 (s)	1692 (s)

The surprising feature of the data (Table I) is the observation that the asymmetric N=N=N stretching absorption, hitherto, always observed as a strong single band[7] now appears as a doublet (Fig. 1). In first observing this for benzazide (IV. Y = C_6H_5-) (curve 2 of Fig. 1) it was thought that the product had decomposed from the time involved in its preparation to the taking of the spectrum and that the doublet was that of phenylisocyanate as reported by Hoyer[9] (at 2277 and 2262 cm.⁻¹). Accordingly, a freshly prepared specimen of benzazide was divided into three portions and one por-

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(1) The authors gratefully acknowledge sponsorship of this research by the Office of Ordnance Research, U. S. Army.

(2) To whom all correspondence should be addressed.

(3) F. L. Scott, *Experienta*, **13**, 275 (1957).

(4) E. Lieber *et. al.*, (a) *J. Org. Chem.*, **22**, 441 (1957); (b) *J. Org. Chem.*, **22**, 1750 (1957); (c) *Can. J. Chem.*, **35**, 832 (1957); (d) *Can. J. Chem.*, **36**, 801 (1958); (e) *Chem. and Ind.*, **1958**, 893.

(5) Private communications from: (a) Professor P. A. S. Smith, University of Michigan; and, (b) Professor K. A. Jensen, University of Copenhagen.

(6) F. L. Scott, A. Koczarski, and J. Reilly, *Nature*, **170**, 922 (1952).

(7) (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1958; (b) E. Lieber *et al.*, *Anal. Chem.*, **29**, 916 (1957).

(8) (a) N. V. Sidgwick, *The Organic Chemistry of Nitrogen*, Oxford Clarendon Press, 1937; (b) P. A. S. Smith, *The Curtius Reaction* in *Organic Reactions*, vol. III, J. Wiley and Sons, Inc., New York, 1946.

(9) H. Hoyer, *Chem. Ber.*, **89**, 2677 (1956).

tion decomposed[8b] to phenylisocyanate and its spectrum taken together with that of its admixture with benzazide. Curves 1, 2, and 3 of Fig. 1 clearly demonstrated that the doublet for benzazide was, indeed, real. Curves 4, 5, and 6 of Fig. 1 show similar doublets for three additional acid azides. Curve 7 is for *m*-nitrophenylisocyanate prepared by decomposition of the *m*-nitrobenzazide. It can be clearly noted from curves 4, 5, and 6 that traces of isocyanate are present in each case. Accordingly, the spectrum between 2500 to 2000 cm.$^{-1}$ serves as a powerful method for establishing the purity of acid azides. The benzazide as finally prepared showed no trace of isocyanate impurity by this method.

References relating to the infrared absorption spectra of organic acid azides are difficult to find since such data that have been noted were incidental insertions in a larger work. Ungnade[10] examined the spectra of a series of α-nitroacetazides ($O_2NCR^1R^2C(O)N_3$ where R^1 and R^2 were H and CH_3) in solution and reported a single band for the N_3 absorption at 2155 cm.$^{-1}$ and 2150 cm.$^{-1}$ No characterizations of the α-nitroacetrazides were attempted. Boyer *et al.*[11] reported a strong singlet N_3 absorption for methane sulfonyl azide at 2137 cm.$^{-1}$ Lucien[12] has reported the azide absorption frequencies at 2180 cm.$^{-1}$ (asym.) and 1350 cm.$^{-1}$ (sym.) for nitrosyl azide.

The present investigation continues particularly with extension to the more sensitive acid azides and to an examination of the effect of increasing conjugation on possible group frequency shifts in organic acid azides.

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[10] H. E. Ungnade and L. W. Kissinger, *J. Am. Chem. Soc.*, **79**, 1662 (1957).

[11] J. H. Boyer *et al.*, *J. Org. Chem.*, **23**, 1051 (1958).

[12] H. W. Lucien, *J. Am. Chem. Soc.*, **80**, 4458 (1958).

Chemistry of Merimines. II. Reductive Alkylation

WILLIAM B. WRIGHT, JR.

Received January 9, 1959

The preparation and properties of a number of derivatives of merimine, 2,3-dihydro-1H-pyrrolo-[3,4-*c*]-pyridine, were described in the first paper of this series.[1] Additional merimine derivatives have now been prepared by the reductive alkylation of 2-unsubstituted merimines.

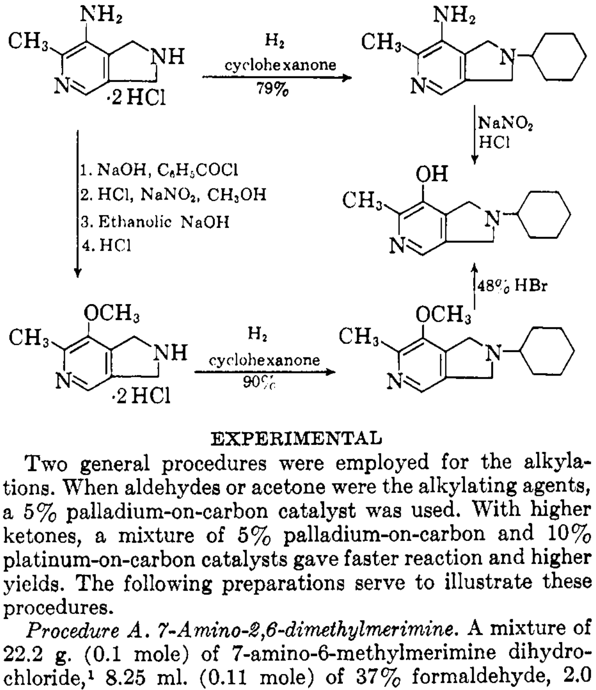
A review by Emerson[2] of the preparation of amines by reductive alkylation states that only poor yields are obtained in the preparation of tertiary amines from aliphatic secondary amines and ketones. It is interesting, therefore, that excellent yields of tertiary amines were obtained when 2-unsubstituted merimine derivatives were reductively alkylated with either aldehydes or ketones.

When the alkylation was stopped after absorption of about 1 molar equivalent of hydrogen, substitution occurred almost entirely in the 2-position even when 7-amino-6-methylmerimine dihydrochloride was alkylated with a large excess of the carbonyl compound. It was possible, however, to prepare a trimethyl derivative of 7-amino-6-methylmerimine dihydrochloride by allowing the alkylation to continue for 29 hr. In this experiment, 7-dimethylamino-2,6-dimethylmerimine dihydrochloride was obtained in 75% yield.

The position of monoalkylation has been established by conversion of 7-amino-2,6-dimethylmerimine dihydrochloride to the corresponding 7-bromo and 7-chloro analogs. These products would not be obtained if the 7-amino group were methylated. In the 2-cyclohexylmerimine series the structure has been proved by the sequence of reactions pictured below.

The preparation of the 7-methoxy-6-methylmerimine dihydrochloride has been previously described.[1]

The compounds prepared are described in Table I.



EXPERIMENTAL

Two general procedures were employed for the alkylations. When aldehydes or acetone were the alkylating agents, a 5% palladium-on-carbon catalyst was used. With higher ketones, a mixture of 5% palladium-on-carbon and 10% platinum-on-carbon catalysts gave faster reaction and higher yields. The following preparations serve to illustrate these procedures.

Procedure A. 7-Amino-2,6-dimethylmerimine. A mixture of 22.2 g. (0.1 mole) of 7-amino-6-methylmerimine dihydrochloride,[1] 8.25 ml. (0.11 mole) of 37% formaldehyde, 2.0 g. of 5% palladium-on-carbon catalyst and 200 ml. of water was shaken in the Parr hydrogenator under hydrogen pressure of about 3 atmospheres until 0.1 mole of hydrogen was absorbed. This usually required less than 30 min. The catalyst was filtered off and the filtrate was concentrated to dryness. The product was washed onto a filter with ethanol and then recrystallized from dilute ethanol. The yield of pure 7-amino-2,6-dimethylmerimine dihydrochloride, m.p. >300°, was 80%.

The base, m.p. 155–157°, was obtained when the dihydrochloride was treated with 2 equivalents of 5*N* sodium hydroxide and the aqueous layer was extracted with chloroform.

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[1] W. B. Wright, Jr., J. S. Webb, and J. M. Smith, Jr., *J. Am. Chem. Soc.*, **79**, 2199 (1957).

[2] W. S. Emerson, *Org. Reactions*, **IV**, 195 (1948).