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.

DEPARTMENT OF CHEMISTRY
DEPAUL UNIVERSITY
CHICAGO 14, ILL.

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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).

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Chemistry of Merimines. II. Reductive Alkylation

WILLIAM B. WRIGHT, JR.

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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.

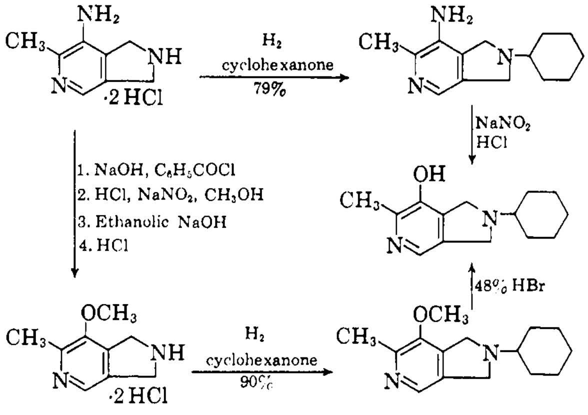
A review by Emerson[2] of the preparation of amines by reductive alkylation states that only poor yields are obtained in the preparation of tertiary amines from aliphatic secondary amines and ketones. It is interesting, therefore, that excellent yields of tertiary amines were obtained when 2-unsubstituted 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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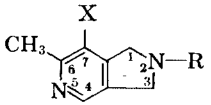
[1] W. B. Wright, Jr., J. S. Webb, and J. M. Smith, Jr., *J. Am. Chem. Soc.*, **79**, 2199 (1957).

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

TABLE I

7-SUBSTITUTED-2-ALKYL-6-METHYLMERIMINES



R	X	Yield, %[a]	Charac-terized As	M.P., °C.[b]	Formula	Carbon, %		Hydrogen, %		Chlorine, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl	NH_2	80[c]	2HCl	>300	$C_9H_{15}Cl_2N_3$	45.8	45.5	6.4	6.5	30.0	29.9	17.8	18.1
			Base	155–157	$C_9H_{13}N_3$	66.2	65.8	8.0	8.2			25.7	25.7
Methyl	Dimethyl-amino	75	2HCl	246 dec.	$C_{11}H_{19}Cl_2N_3$	50.0	49.6	7.3	7.5	26.8	26.9	15.9	15.8
Methyl	OH	80[c]	2HCl	246–248	$C_9H_{14}Cl_2N_2O$	45.6	45.6	6.0	6.3	29.9	29.5	11.8	11.9
Methyl	Cl	33[d]	2HCl	264 dec.	$C_9H_{13}Cl_3N_2$	42.3	42.2	5.1	5.3	41.6	41.4	11.0	11.1
Methyl	Br	43[d,e]	2HCl	269 dec.	$C_9H_{13}BrCl_2N_2$	36.0	35.8	4.4	4.5	23.6	23.5	9.3	9.6
2-Propyl	NH_2	88[c,f]	2HCl	>300	$C_{11}H_{19}Cl_2N_3$	50.0	50.0	7.2	7.3	26.8	27.1	15.9	16.3
1-Butyl	NH_2	88[c,g]	Base[h]	128–130	$C_{12}H_{19}N_3$	70.2	70.3	9.3	9.5			20.5	20.2
			2HCl	>300	$C_{12}H_{21}Cl_2N_3$	51.8	52.1	7.6	7.9	25.4	25.7	15.2	15.5
3-Pentyl	NH_2	67[i]	Base[h]	119–121	$C_{13}H_{21}N_3$	71.2	70.9	9.7	9.8			19.2	19.6
Cyclohexyl	NH_2	79[i,j]	Base	181–182	$C_{14}H_{21}N_3$	72.7	72.8	9.2	9.3			18.2	18.5
			2HCl	>300	$C_{14}H_{23}Cl_2N_3$	55.3	55.0	7.6	7.7	23.3	23.5	13.8	13.7
Cyclohexyl	OCH_3	90[i]	2HCl	216 dec.	$C_{15}H_{24}Cl_2N_2O$	56.4	56.1	7.6	7.8	22.2	21.9	8.8	8.8
Cyclohexyl	HO	100[k,l]	2HBr	320 dec.	$C_{14}H_{22}Br_2N_2O$	42.7	42.7	5.6	5.9			7.1	7.3
		50[d]	Base	253–255	$C_{14}H_{20}N_2O$	72.4	72.2	8.7	8.9			12.1	11.8

[a] Unless otherwise noted, yields are after recrystallization. [b] Melting points are uncorrected. [c] Procedure A. [d] By diazotization of the 7-amino analog. [e] Bromine: calcd. 26.6, found 26.7. [f] Used 2 equivalents of acetone. [g] Used 2 equivalents of butyraldehyde and isolated as the base. [h] Recrystallized from ethyl acetate. [i] Procedure B. [j] Crude yield, m.p. 178–180°, was 97%. [k] By cleavage of the 7-methoxy analog. [l] Yield before recrystallization.

Procedure B. 7-Amino-2-cyclohexyl-6-methylmerimine. A mixture of 22.2 g. (0.1 mole) of 7-amino-6-methylmerimine dihydrochloride, 25 ml. (0.24 mole) of cyclohexanone, 2 g. of 5% palladium on carbon catalyst, 2 g. of 10% platinum-on-carbon catalyst and 230 ml. of water was shaken in the Parr hydrogenator under hydrogen pressure of about 3 atmospheres until about 0.13 mole of hydrogen was absorbed. The catalyst was filtered off, and the filtrate was concentrated and then treated with 25 ml. of 50% potassium hydroxide. The crystals which separated were filtered, washed with water, and dried. The crude yield of 7-amino-2-cyclohexyl-6-methylmerimine, m.p. 178–180°, was 97%. On recrystallization from ethanol, a 79% yield of pure product, m.p. 181–182°, was obtained.

When the above base was treated with two equivalents of ethanolic hydrogen chloride, 7-amino-2-cyclohexyl-6-methylmerimine dihydrochloride, m.p. 300°, was obtained. This compound was purified by recrystallization from dilute ethanol.

7-Chloro-2,6-dimethylmerimine dihydrochloride. A solution of 7.25 g. of sodium nitrite in 60 ml. of water was added over 5 min. to a mixture of 23.6 g. (0.1 mole) of 7-amino-2,6-dimethylmerimine dihydrochloride, 100 ml. of 4*N* hydrochloric acid and 600 ml. of water. The reaction mixture was held at 0 to −2° during this addition and for 10 min. longer and then poured into a mixture of 10 g. of cuprous chloride and 150 ml. of 4*N* hydrochloric acid. The mixture was allowed to warm up to 30° over a 3-hr. period and was then treated with hydrogen sulfide. The precipitate was filtered off and the filtrate was treated with activated charcoal. The clear solution was concentrated to dryness and the product was washed onto a filter with ethanol. The yield of salt and crude product was 20.1 g. The estimated product was 14.3 g. (56%). This mixture was stirred with 6.2 g. of sodium methylate and 400 ml. of ethanol for 2 hr. The salt was filtered off and the filtrate was treated with activated carbon and then concentrated to dryness. On addition of alcoholic hydrogen chloride, a precipitate separated. This product was filtered off and recrystallized twice from 90% ethanol. The yield, including recoveries, of pure 7-chloro-2,6-dimethylmerimine dihydrochloride, m.p. 264° dec., was 8.1 g. (33%).

7-Bromo-2,6-dimethylmerimine dihydrochloride. A mixture of 23.6 g. (0.1 mole) of 7-amino-2,6-dimethylmerimine dihydrochloride, 11.2 g. of sodium methylate and 400 ml. of anhydrous ethanol was stirred at room temperature for 2 hr. and then filtered to remove the salt. The filtrate was concentrated under reduced pressure to a white solid. A mixture of 400 ml. of water and 50 ml. of 40% hydrobromic acid was added and the solution was cooled to −2°. A solution of 7.25 g. of sodium nitrite in 60 ml. of water was added over a 5-min. period at 0 to −2°. The reaction mixture was held at this temperature for 10 more min. and then poured into a cold mixture of 17.5 g. of cuprous bromide, 70 ml. of 40% hydrobromic acid and 40 ml. of water. After 19 hr., hydrogen sulfide was passed in and the dark precipitate was filtered off. The filtrate was treated with activated carbon, concentrated to dryness, and the product was washed onto a filter with ethanol. The dried filter cake was added to an excess of 5*N* sodium hydroxide and extracted with chloroform. After drying over magnesium sulfate, the chloroform layer was mixed with 37 ml. of 4*N* ethanolic hydrogen chloride and the product which separated was filtered off and recrystallized from 90% ethanol. The yield of 7-bromo-2,6-dimethylmerimine dihydrochloride, m.p. 269° dec., was 43%.

7-Dimethylamino-2,6-dimethylmerimine dihydrochloride. A mixture of 22.2 g. (0.1 mole) of 7-amino-6-methylmerimine dihydrochloride, 40.5 g. (0.5 mole) of 37% formaldehyde, 160 ml. of water and 2 g. of 10% palladium-on-carbon catalyst was shaken in the Parr hydrogenator under an initial hydrogen pressure of about 3 atmospheres. Hydrogen absorption was rapid at first and 0.1 mole was absorbed in 25 min. The reaction rate then dropped sharply and the absorption was only 0.23 moles at the end of 22 hr. An additional 2 g. of 10% palladium-on-carbon catalyst was added and the reduction was continued until the total hydrogen absorption was 0.3 moles. The total reaction time was 29 hr. The reaction mixture was filtered, concentrated, treated with aqueous sodium hydroxide, and extracted with chloroform. The chloroform layer was distilled and the portion which boiled at 102–108° (0.2 mm.), n_D^{23} 2.544, was collected. This oil was treated with ethanolic hydrogen chloride and ether, and the crystals which separated were recrystallized from ethanol by the addition of ether. The yield of pure 7-dimethylamino-2,6-dimethylmerimine dihydrochloride, m.p. 246° dec., was 19.7 g. (75%).

2-Cyclohexyl-7-hydroxy-6-methylmerimine. (A) *From 7-amino-2-cyclohexyl-6-methylmerimine.* A solution of 3.8 g. of sodium nitrite in 30 ml. of water was added over a 30-min. period at 93–97° to a rapidly stirred solution of 11.5 g. (0.05 mole) of 7-amino-2-cyclohexyl-6-methylmerimine in 600 ml. of 0.05*N* hydrochloric acid. The reddish solution was held at the same temperature for 20 min. longer and then treated with activated carbon. The filtrate was concentrated to about 100 ml. and treated with excess sodium carbonate. The tan product which separated was filtered and washed with water, and the moist cake was recrystallized twice from ethanol. The yield of 2-cyclohexyl-7-hydroxy-6-methylmerimine, m.p. 253–255°, was 3.7 g. (32%). Recoveries from the alcoholic filtrates increased the yield to 50%.

(B) *From 2-Cyclohexyl-7-methoxy-6-methylmerimine.* A solution of 2.0 g. of 2-cyclohexyl-7-methoxy-6-methylmerimine, m.p. 58–60° but not analyzed, in 20 ml. of 48% hydrobromic acid was heated on the steam bath for 30 hr. and then concentrated to dryness. The residue was washed onto a filter with ethanol and dried. The yield of 2-cyclohexyl-7-hydroxy-6-methylmerimine dihydrobromide, m.p. *ca.* 320° dec., was 3.2 g. (100%). Recrystallization from ethanol improved the color but did not change the decomposition point.

When the dihydrobromide was dissolved in water and treated with sodium carbonate, the base was obtained. After recrystallization from ethanol it was identical by melting point, mixture melting point, and infrared spectra to the 2-cyclohexyl-7-hydroxy-6-methylmerimine prepared by method A above.

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ORGANIC CHEMICAL RESEARCH SECTION
LEDERLE LABORATORIES DIVISION
AMERICAN CYANAMID CO.
PEARL RIVER, N. Y.

Alkyl *N*,*N*-Dialkyl Methylphosphonamidates[1]

DAVID G. COE,[2] B. J. PERRY, AND E. S. SHERLOCK

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In a series of recent publications Razumov *et al.*[3] describe the preparation and biological properties of

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(2) Present address: Jackson Laboratory, Box 525, Wilmington 99, Del.

(3) A. I. Razumov, O. A. Mukhacheva, and E. A. Markovich, *Khim. i Primenie Fosfororgan. Soedinenii, Akad. Nauk S.S.S.R., Trudy l-oi Konferents.*, 194 (1955) (published 1957); and *Zhur. Obschei Khim.*, **27**, 2389 (1957); A. I. Razumov, *Trudy Kazan. Khim. Technol. Inst. im. S. M. Kirova*, **23**, 205 (1957).