Method of Preparation of Positive Iodine Salts.—The reaction of the silver carboxylates with iodine was carried out as previously reported,[1] except that the chloroform filtrate in which the positive iodine salt was dissolved was treated with three volumes of Skellysolve A and permitted to cool in a Dry Ice chest for 48 hours. The crystalline salts were filtered, washed with dry ether, and dried *in vacuo* over sulfuric acid.

Formation of Iodopyridines.—A positive iodine salt[3] was refluxed in dry ether for 72 hours. The mixture was then filtered and the residue washed with dry ether and discarded. Any iodine present in the combined ether solutions was removed by treatment with aqueous thiosulfate. The ether solution was then extracted with sodium carbonate solution, washed with water and extracted with 20% HCl. The acid extract was concentrated and cooled, and treated with gaseous ammonia until precipitation occurred. Sublimation of the filtered precipitate gave colorless needles of **3-iodopyridine**, m. p. 53–54°, which with chlorine readily formed the yellow iodochloride, m. p. 127–129°. Yields of pure 3-iodopyridine obtained in typical runs were as follows: A, from 280 g. of silver *o*-chlorobenzoate, 1.6 g. (0.8%); B, from 76 g. of monopyridine iodine (I)-*o*-chlorobenzoate, 1.2 g. (2.7%); C, from 237 g. of silver *m*-chlorobenzoate, 1.2 g. (0.6%). Because of the extreme volatility of 3-iodopyridine, it is probable that the amounts isolated were considerably smaller than those actually formed in the reaction.

On standing, the filtrate remaining after removal of the 3-iodopyridine in C deposited 0.9 g. (0.3%) of **3,5-diiodopyridine**, m. p. after recrystallization from high boiling petroleum ether 172–172.8°. The hydrochloride melted at 193.9–194.7°.[4]

5-Iodo-2-methylpyridine.—In one experiment in which α-picoline was used in place of pyridine, 127 g. of silver *m*-chlorobenzoate gave a basic fraction from which there was isolated 1.4 g. (1.7%) of **5-iodo-2-methylpyridine**, a heavy oil, b. p. 205–210°. The picrate melted at 149°.[5]

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(3) The same results were obtained if, in place of the positive iodine salt, one used the residue isolated by removal of silver iodide and evaporation of the solvent from the mixture obtained in the reaction of a silver carboxylate with iodine in the presence of pyridine in chloroform solution.

(4) Baumgarten, *Ber.*, **72B**, 567 (1939), reported a m. p. of 171.5° for 3,5-diiodopyridine and of 195–196° for the hydrochloride.

(5) Plazek and Rodewald, *Roczniki Chem.*, **21**, 150 (1947) [*C. A.*, **42**, 5456b (1948)] reported the b. p. of 5-iodo-2-methylpyridine as 205–215° and the m. p. of the picrate as 150°.

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NEW COMPOUNDS

Allophanates[1,2]

These allophanates were prepared in order to establish them as easily made derivatives for the alcohols. The procedure employed was to depolymerize cyanuric acid in a slow stream of carbon dioxide at 360–400° by means of an electrically operated heater and to pass the cyanic acid

TABLE I

ALLOPHANATES, ROCONHCONH$_2$

R	Alcohol B. p. °C.	Alcohol B. p. Mm.	n^{25}D	M. p., °C.	Solvents for recrystn.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
d,l-iso-$C_3H_7CH(CH_3)$–	111.5–112.0	760	1.4071 1.4091(20)	163[a]	Acetone(2×) Ethanol	$C_7H_{14}N_2O_3$	48.26	48.56	8.10	8.24	16.08	15.8 15.8
$(C_2H_5)_2CHCH_2$–	147.7	751	1.4200	161.0–161.5[b]	Ethanol(3×) Acetone(2×)	$C_8H_{16}N_2O_3$	51.04	51.09 50.84	8.57	8.47 8.70	14.89	14.94
(iso-$C_3H_7)_2CH$–	138	762	1.4214 1.4230(20)	173.5–174.5	Ethanol(2×) Acetone(2×)	$C_9H_{18}N_2O_3$	53.44	53.42	8.97	8.97	13.85	13.70
t-$C_4H_9CH_2CH(CH_3)CH_2CH_2$–	191	752	1.4308	148.5–149.0	Ethanol(2×)	$C_{11}H_{22}N_2O_3$	57.36	57.11 57.06	9.63	9.63 9.65	12.17	12.17
n-$C_{14}H_{29}$–	M. p. 38			156.0–156.5	Ethanol(2×) Acetone(2×)	$C_{16}H_{30}N_2O_3$	63.96	64.00 63.66	10.74	10.59 10.51	9.33	9.49

[a] Ref. 5 reports 169–170°. [b] Ref. 5 reports 156–158°.

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(1) Taken from a thesis by H. W. B. for the B.S. degree, Polytechnic Institute of Brooklyn, June, 1950.

(2) A review of the literature including methods of preparation, a detailed experimental procedure, and a list of 297 known allophanates may be obtained in Document 2858 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.65 for 35 mm. microfilm or $6.30 for photocopies (6 × 8 inches).

into about 1 ml. of the alcohol.[3,4,5] After washing the allophanate with ether, it was recrystallized to constant melting point. Myristyl alcohol was first dissolved in a few milliliters of benzene.

Purification of the Alcohols.—The alcohols were dried over solid potassium hydroxide, filtered and distilled through a Pyrex column (2.2 × 75 cm.), packed with $^1/_8$-in. single turn Pyrex helices, and equipped with a total reflux partial take-off distilling head. A constant boiling middle cut was taken for conversion to the allophanate. Myristyl alcohol was recrystallized twice from benzene and twice from methanol to constant melting point.

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(3) J. Liebig and F. Wöhler, *Ann. Physik*, **20**, 369 (1830); *Ann.*, **59**, 291 (1846).

(4) A. Béhal, *Bull. soc. chim.*, [4] **25**, 373 (1919).

(5) M. A. Spielman, J. D. Barnes and W. J. Close, THIS JOURNAL, **72**, 2520 (1950).

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Bis-(β-chloroethyl)-cyclohexylamine Hydrochloride[1]

Bis-(β-hydroxyethyl)-cyclohexylamine[2,3] (5.14 g., 0.027 mole) was converted to the hydrochloride by addition of concentrated hydrochloric acid (10 ml.). The excess acid and water were removed under reduced pressure. The residual oil was covered with benzene (10 ml.) and 4.9 ml. (0.068 mole) of thionyl chloride was added dropwise. After refluxing for ten minutes and cooling, a crystalline product separated. This crystalline material was removed by filtration and washed with acetone to give a crude yield of 5.75 g. (80.5%). One crystallization from acetone (61 ml./g.) failed to raise the melting point above that of the original of 176–178° (dec.).

Anal. Calcd. for $C_{10}H_{20}Cl_3N$: C, 46.08; H, 7.73; Cl, 40.81; N, 5.38. Found: C, 46.57; H, 7.62; Cl, 40.84; N, 5.54.

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(1) Bis-(β-chloroethyl)-cyclohexylamine and its hydrochloride have been mentioned in a table of vapor pressures by C. E. Redemann, *et al.*, THIS JOURNAL, **70**, 1648 (1948), but physical constants and analyses have not been published.

(2) J. P. Bain and C. B. Pollard, *ibid.*, **61**, 2704 (1939).

(3) F. F. Blicke and C. E. Maxwell, *ibid.*, **64**, 428 (1942).

CONTRIBUTION FROM THE
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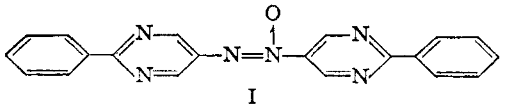
2,2′-Diphenyl-5,5′-azoxypyrimidine

A solution of 1.00 g. of 5-nitro-2-phenylpyrimidine[1] in 25 ml. of dioxane was shaken for 25 minutes with 2 g. of one-year-old Raney nickel under a hydrogen pressure of 2 atmospheres. Concentration of the solution gave 0.34 g. (40% yield) of 2,2′-diphenyl-5,5′-azoxypyrimidine (I). Upon recrystallization from dioxane it was obtained in the form of fine, yellow needles, m. p. 303–305°.

Anal.[2] Calcd. for $C_{20}H_{14}N_6O$: C, 67.78; H, 3.98; N, 23.72. Found: C, 67.78; H, 3.81; N, 23.90.



I

The analytical values agree very closely with the empirical formula corresponding to structure I and are significantly different from the calculated values for other possible reduction products, such as the amine, the nitroso compound or the corresponding azo-compound. Further evidence for structure I is provided by a comparison of the ultraviolet absorption spectrum with that of azobenzene and azoxybenzene, Fig. 1. The spectrum of I has no maximum in the visible region, and in this respect resembles the spectrum of azoxybenzene rather than that of azobenzene.

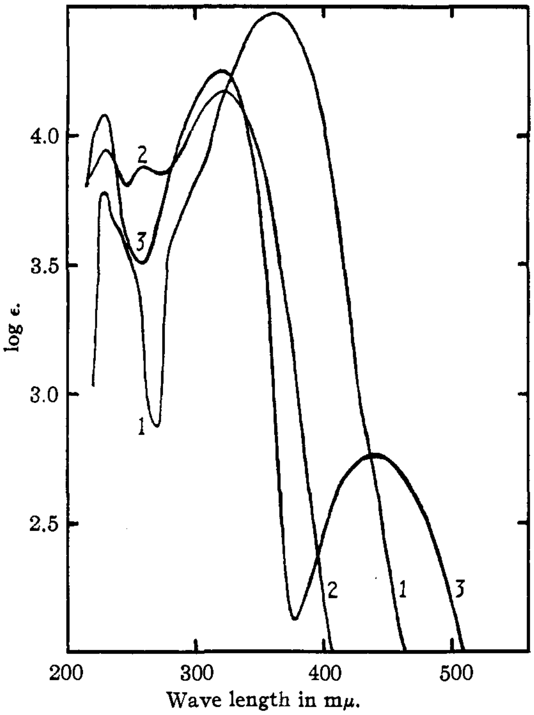


Fig. 1.—Molar extinction curves in 95% ethanol: (1) 2,2′-diphenyl-5,5′-azoxypyrimidine (I); (2) azoxybenzene; (3) azobenzene.

The only precedent found for this unexpected reduction product is a report[3] that nitrobenzene and several of its derivatives were deoxygenated by mixing with Raney nickel in an open beaker to give 35 to 50% yields of azo- and azoxybenzenes.

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(1) Hale and Brill, THIS JOURNAL, **34**, 91 (1912).

(2) Analysis by Micro-Tech Laboratories, Skokie, Illinois.

(3) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

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Some Derivatives of Nitroguanidine[1]

The compounds listed in the Table I were prepared by the methods of McKay and Wright,[2] and McKay,[3] from 1-methyl-1-nitroso-3-nitroguanidine and the appropriate primary amine or hydrazine; they were recrystallized from aqueous ethyl alcohol.

1-Acetamido-3-nitroguanidine. Method A.—A solution of 11.9 g. of nitroaminoguanidine (0.1 mole), 30 ml. of glacial acetic acid and 10 ml. of acetic anhydride was

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(1) All melting points are corrected. The analyses were performed by Mr. Cliff Holford, Analytical Section, Chemistry Division, U. S. Naval Ordnance Test Station, and by Dr. Adalbert Elek, Los Angeles, California.

(2) McKay and Wright, THIS JOURNAL, **69**, 3028 (1947).

(3) McKay, *ibid.*, **71**, 1968 (1949).