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).

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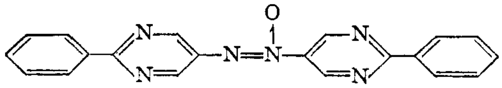
2,2′-Diphenyl-5,5′-azoxypyrimidine

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.

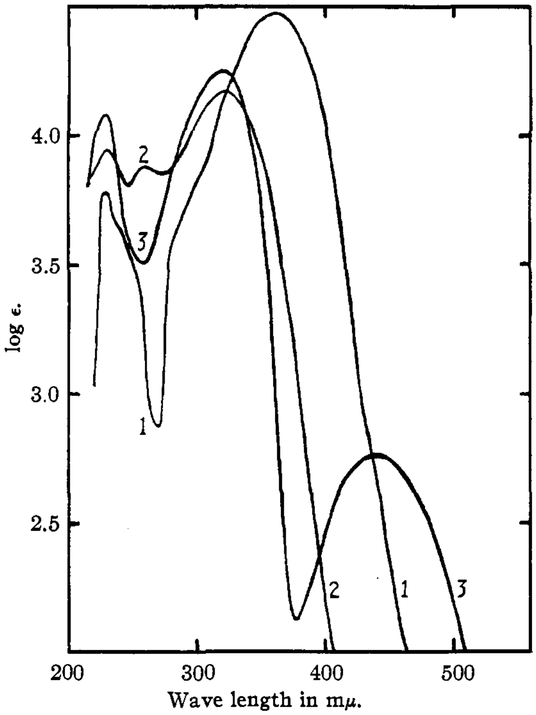


Fig. 1.—Molar extinction curves in 95% ethanol: (1) 2,2′-diphenyl-5,5′-azoxypyrimidine (I); (2) azoxybenzene; (3) azobenzene.

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).

TABLE I

SUBSTITUTED NITROGUANIDINES $RNHC(NH)NHNO_2$

R	Yield, %	Formula	M. p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Carbethoxymethyl	63.3	$C_5H_{10}O_4N_4$	153.5–154.5	31.58	31.54	5.30	5.20	29.46	29.15
2-Aminophenyl	64.6	$C_7H_9O_2N_5$	195–197 dec.[a]	43.07	43.34	4.65	4.66	35.88	35.80
4-Aminophenyl	78.9	$C_7H_9O_2N_5$	219–220 dec.	43.07	43.53	4.65	4.80	...	...
Anilino	96	$C_7H_9O_2N_5$	168	43.07	43.08	4.65	3.98	35.88	35.99
Pyridyl-2	..	$C_6H_7O_2N_5$	229 dec.	39.78	40.08	3.90	3.83	...	...
5-Methylpyridyl-2	41.1	$C_7H_9O_2N_5$	219	43.07	43.04	4.65	4.57	...	...
6-Methylpyridyl-2	15.4	$C_7H_9O_2N_5$	204–205	43.07	43.9	4.65	4.48	...	...

[a] Compound does not melt up to 250° if heated slowly from room temperature; decomposes at indicated temperature when plunged into hot-bath.

heated for two hours at 85–90°, after which it was cooled in an ice-bath. When 100 ml. of diethyl ether was added, a fine white precipitate formed which was removed by filtration and washed with four 20-ml. portions of ether. The yield of dried product was 15.7 g. (97.5%); m. p. 189–190° (dec.). When 9.0 g. was recrystallized from 150 ml. of water, 6.0 g. of highly refractive, transparent needles was recovered; m. p. 195° (dec.). This compound does not form a hydrazone with benzaldehyde. *Anal.* Calcd. for $C_3H_7O_3N_5$: C, 22.36; H, 4.38; hydrazino N, 17.39. Found: C, 22.73; H, 4.24; hydrazino N by the Jamieson method, 17.47.

Method B.—From 0.02 molar quantities of acethydrazide and methyl nitrosonitroguanidine, reacting according to the procedure of McKay and Wright,[2] there was obtained 2.34 g. (73%) of impure acetamidonitroguanidine decomposing at 174–177°. One recrystallization from water, followed by two recrystallizations from 95% ethyl alcohol, gave needles and prisms, decomposing at 194–195°. A mixed melting point with the product made by the above procedure was 196°. *Anal.* Calcd. for $C_3H_7O_3N_5$: hydrazino N, 17.39. Found: hydrazino N by the Jamieson method, 17.36.

3-Methyl-5-nitroamino-1,2,4-triazole.—A solution of 3.6 g. of 1-acetamido-3-nitroguanidine and 2.4 g. of anhydrous sodium carbonate in 35 ml. of water was heated on a steam-bath for twenty-five minutes according to the procedure of Thiele and Heidenreich.[4] After the solution had been cooled in an ice-bath, it was acidified with concentrated hydrochloric acid and allowed to stand overnight at 0°. The product was removed by filtration, washed with a small volume of cold water, and air-dried. The yield was 3.1 g. (97%); m. p. 201–202°. Two recrystallizations from water gave rosettes of colorless needles; m. p. 212–213° (dec.). *Anal.* Calcd. for $C_3H_5O_2N_5$: C, 25.18; H, 3.52; N, 48.94. Found: C, 25.44; H, 3.44; N, 48.65.

1-Formamido-3-nitroguanidine.—The amide was obtained by heating nitroaminoguanidine with three times its weight of 90% formic acid for 1.5 hours at 85–90°, followed by cooling, filtration, and washing with cold water to remove the excess formic acid. Two recrystallizations from water gave long thin needles; m. p. 191–192° (dec.). *Anal.* Calcd. for $C_2H_5O_3N_5$: N, 47.61; hydrazino N, 19.05; acid value, 381.4. Found: N, 47.73, 47.70; hydrazino N by the Jamieson method, 19.22, 18.99; acid value, 374.7.

5-Nitroamino-1,2,4-triazole.—Using the same procedure as employed for the preparation of 3-methyl-5-nitroamino-1,2,4-triazole, an 85% yield was obtained from 5 g. of formamidonitroguanidine. The white, granular product decomposed at 217° after one recrystallization from water; it does not give a hydrazine nitrogen titration by the Jamieson method. *Anal.* Calcd. for $C_2H_3N_5O_2$: C, 18.61; H, 2.34; N, 54.26. Found: C, 18.08, 18.82; H, 2.50, 2.31; N, 53.91, 53.96.

N-Nitroguanyl Benzenesulfonamide.—A cold solution of 28.0 g. of 85% potassium hydroxide (0.4 mole) in 60 ml. of water was added to a suspension of 20.8 g. of nitroguanidine (0.2 mole) in 300 ml. of acetone at 25°. When the solution had been cooled to 15°, 39.0 g. of benzenesulfonyl chloride (0.22 mole) was added during thirty-five minutes with good agitation. The temperature was maintained at 15 to 20°. Toward the end of the addition a saturated solution of potassium hydroxide was slowly added in order to keep the solution alkaline. The solution was finally stirred for three hours. The monopotassium salt of the sulfonamide separated as a white, granular solid, which was removed by filtration and washed with two 50-ml. portions of water. The yield was 45.4 g. (80.5%); m. p. 218–219° (dec.). When 20 g. was recrystallized from 400 ml. of 75% ethyl alcohol, 15.8 g. was recovered as large, coarse plates; m. p. 219.5–220.5° (dec.). *Anal.* Calcd. for $C_7H_7O_4N_4SK$: C, 29.67; H, 2.49; N, 19.78; K, 13.80. Found: C, 29.88; H, 2.80; N, 19.85; K, 13.51.

The free sulfonamide was prepared by dissolving 21.8 g. of the potassium salt in 200 ml. of water at 60° and adding 8 ml. of concentrated hydrochloric acid. The white precipitate which formed was removed by filtration (after the solution was cooled to 0°) and washed with two 20-ml. portions of water. The recovery was 97%. The product crystallized from 100 ml. of 95% ethyl alcohol as rosettes of coarse prisms; m. p. 149–150.5° (dec.). *Anal.* Calcd. for $C_7H_8O_4N_4S$: N, 22.94. Found: N, 23.21.

1-Benzoyl-3-nitroguanidine.—A slurry of 20.8 g. of nitroguanidine (0.2 mole), 41.0 g. of potassium hydroxide and 330 ml. of water was cooled to 2° with agitation and treated during one hour with 42.2 g. of benzoyl chloride (0.3 mole). The temperature was maintained between 9 and 11°. Agitation was then continued for two hours at the same temperature after which the solution was neutralized with concentrated hydrochloric acid. The product was removed by filtration after the mixture had stood overnight at 0° and washed with two 100-ml. portions of water. The wet cake was then heated to boiling with 400 ml. of water, filtered, and re-extracted with 100 ml. more of boiling water. The yield of air-dried, water insoluble material was 5.9 g. (14.2%); m. p. 214–216° (dec.). One recrystallization from 565 ml. of 80% alcohol gave flat plates and needles decomposing at 218.5–219.5°. *Anal.* Calcd. for $C_8H_8O_3N_4$: C, 46.15; H, 3.87; N, 26.92. Found: C, 46.03; H, 3.93; N, 26.49.

1-Benzenesulfonamido-3-nitroguanidine.—When 3.53 g. of benzenesulfonyl chloride was added all at once to a suspension of 2.38 g. of nitroaminoguanidine in 25 ml. of pyridine, the mixture warmed spontaneously to about 60° and all the solid dissolved. The solution was then heated for ten minutes at 55–60°, after which it was allowed to stand for one hour at room temperature. The product was precipitated by pouring into 125 ml. of water and chilling. The yield was 2.9 g. (56%); m. p. 190–191° (dec.). Recrystallization from 180 ml. of 33% ethyl alcohol gave needles, m. p. 194–195° (dec.). *Anal.* Calcd. for $C_7H_9O_4N_5S$: N, 27.02. Found: N, 26.86, 26.75.

1-Benzamido-3-nitroguanidine. Method A.—The same procedure was employed as in the preparation of 1-benzenesulfonamido-3-nitroguanidine except that 2.80 g. of benzoyl chloride was used. The yield was 2.2 g. (49.3%); m. p. 190–191° (dec.). Recrystallization from 180 ml. of

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[4] Thiele and Heidenreich, *Ber.*, **26**, 2599 (1893).

33% ethyl alcohol raised the decomposition point to 197°; colorless, flat pointed needles. *Anal.* Calcd. for $C_8H_9O_3N_5$: C, 43.05; H, 4.06; N, 31.38. Found: C, 42.96; H, 4.21; N, 31.50.

Method B.—From 0.5 g. of methylnitrosonitroguanidine and 0.45 g. of benzhydrazide in 10 ml. of 50% ethyl alcohol, there was recovered 0.6 g. of compound (90%), decomposing at 197.5°. A mixed melting point with the compound made by the above procedure was the same.

1-(4-Nitrobenzamido)-3-nitroguanidine. Method A.—The same procedure was employed as in the preparation of 1-benzenesulfonamido-3-nitroguanidine except that 3.71 g. of *p*-nitrobenzoyl chloride was used. The yield was 1.5 g. (28%). One recrystallization from 375 ml. of 76% ethyl alcohol gave a product identical with that prepared by the following method.

Method B.—From the reaction of 0.01 molar quantities of methylnitrosonitroguanidine and *p*-nitrobenzhydrazide in 140 ml. of 70% ethyl alcohol, there was recovered after three days at room temperature 2.15 g. (80%) of a compound decomposing at 193°. Recrystallization from 75% ethyl alcohol gave small, pale yellow needles decomposing at 195.5–196.5°. *Anal.* Calcd. for $C_8H_8O_5N_6$: N, 31.34. Found: N, 31.62.

Ethyl N-Nitroguanidocarbamate.—To a slurry of 3.94 g. of methylnitrosonitroguanidine in 10 ml. of water and 5 ml. of ethyl alcohol was added 2.10 g. of ethyl hydrazinocarbonate. There was an immediate and rapid evolution of gas. After the mixture had remained several days at 0°, the white solid was removed by filtration and washed with three 5-ml. portions of cold water. The yield was 4.0 g. After two recrystallizations from a minimum volume of water, the melting point was 203–203.5° (dec.). This compound does not form a hydrazone with benzaldehyde. *Anal.* Calcd. for $C_4H_9O_4N_5$: C, 25.13; H, 4.74; hydrazino N, 14.66. Found: C, 24.62; H, 4.63; hydrazino N by the Jamieson method, 14.66.

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RECEIVED JUNE 15, 1950

Cetyl Chloro- and Iodoacetates

Cetyl Chloroacetate.—Into a 500-ml. flask were placed 48.4 g. (0.20 mole) of cetyl alcohol and 30.0 g. (20.0 ml., 0.26 mole) of chloroacetyl chloride. The reactants were heated gently with a free flame under reflux for two hours. The reaction mixture was then distilled under reduced pressure, the product collected at 218–220° (10 mm.), which crystallized on cooling to a white wax-like solid m. p. 31°. The yield amounted to 45 g. (70%).

Anal. Calcd. for $C_{18}H_{35}O_2Cl$: Cl, 11.12. Found: Cl, 11.08.

Cetyl Iodoacetate.—A solution of 6.38 g. (0.020 mole) of cetyl chloroacetate in 25 ml. of acetone[1] was mixed with a solution of 4.00 g. (0.027 mole) of sodium iodide in 25 ml. of acetone. The mixture was refluxed one hour and the reaction mixture poured into 300 ml. of ice-cold water. The crude product filtered off and crystallized from alcohol (12 ml./g.) by cooling in ice–salt freezing mixture gave a white crystalline product, 7.5 g. (92%), m. p. 28°. For analysis a further recrystallization from alcohol gave product m. p. 28.5°.[2]

Anal. Calcd. for $C_{18}H_{33}O_2I$: I, 30.94. Found: I, 30.60.

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RECEIVED AUGUST 2, 1950

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[1] Finkelstein, *Ber.*, **43**, 1538 (1910).

[2] Product decomposed on distillation at 4 mm.

1,1,1-Trichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethane and its Dehydrohalogenation Product

1,1,1-Trichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethane.—Fifty grams (0.123 mole) of 1,1,1-trichloro-2,2-bis-(3-carboxy-4-hydroxyphenyl)-ethane,[1] prepared by the condensation of chloral and salicylic acid with sulfuric acid, and 300 ml. of glacial acetic acid, were heated to reflux while concentrated nitric acid was added slowly. After 15 ml. of nitric acid had been added, the solid material had dissolved. A total of 50 ml. of nitric acid was added over a one-hour period at the reflux temperature. The reaction mixture was allowed to stand overnight at room temperature. The precipitated yellow crystals were filtered off to give 43 g. (70%) of the dinitro derivative, m. p. 241–243°. Recrystallization did not raise the melting point.

Assignment of the 5-position to the nitro groups entering the ring is based on the well-known orienting influence of the substituents already present in the ring and on the observed positions of nitration of other related types.[2,3]

Anal. Calcd. for $C_{16}H_9Cl_3N_2O_{10}$: Cl, 21.5; N, 5.66. Found: Cl, 21.6 and 21.3; N, 5.79.

1,1-Dichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethylene.—Five and one half grams (0.011 mole) of 1,1,1-trichloro-2,2-bis-(3-carboxy-4-hydroxy-5-nitrophenyl)-ethane was added to a solution of 20 g. of potassium hydroxide in 750 ml. of water. The mixture was heated to boiling for a few minutes and then acidified with hydrochloric acid. The precipitated solid was separated and recrystallized from a mixture of nitrobenzene and petroleum ether. Four grams (78%) of the yellow crystals of the dehydrohalogenated product, melting at 235–237°, was obtained.

Anal. Calcd. for $C_{16}H_8Cl_2N_2O_{10}$: Cl, 15.5. Found: Cl, 15.5, 15.7.

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[1] Calvet and Mejuto, *J. Chem. Soc.*, 554 (1936).

[2] Shirley, Goreau and Eiseman, THIS JOURNAL, **71**, 3173 (1949).

[3] Forrest, Stephenson and Waters, *J. Chem. Soc.*, 335 (1946).

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RECEIVED MAY 18, 1950

Some Bis-(aryloxy)-methanes

The new compounds were prepared by the reaction of dichloromethane with the sodium salt of the phenol.[1,2] The yields, based on single experiments, are not necessarily the best that could be obtained. The properties and analyses of the compounds prepared are summarized in Table I. These compounds have been tested against the two-spotted spider mite and Mexican bean beetle.[3] The general method of preparation is illustrated by a specific example.

Bis-(2-allyl-4,6-dichlorophenoxy)-methane.—A mixture of 154 g. (0.76 mole) of 2-allyl-4,6-dichlorophenol, 36 g. (0.42 mole) of dichloromethane, 35 g. (0.85 mole) of 97% NaOH, and 200 ml. of methanol were placed in a KA_2S bomb, having a volume of 2 l. and a working capacity of 1.2 l., and heated to 130–140° for 12 hours with a pressure of 100–200 p.s.i.g. The contents were then cooled to room temperature and the material was dumped into a beaker. The bomb was washed out with two 500-ml. portions of distilled water and then with 500 ml. of chlorobenzene. The reaction mixture and washings were placed together and separated in a separatory funnel. The oil layer was then washed twice with 250-ml. portions of water. The aqueous layers were combined and titrated for chlorides to determine the conversion, which was 94%. The oil

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[1] Moyle, U. S. Patent 2,330,234, September 28, 1943.

[2] Britton, Monroe and Hand, U. S. Patent 2,493,711, January 3, 1950.

[3] Kenaga and Hummer, *J. Econ. Entomol.*, **42**, 998 (1949).