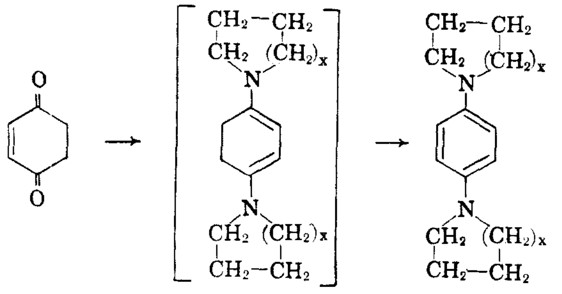
stability usually associated with an enamine function. Analysis suggested the composition $C_{14}H_{22}N_2$ and therefore the bis-enamine structure IIa, but attempted purification at this stage resulted in oxidative transformation. Intentional air-oxidation yielded the benzenoid product, 1,1'-*p*-phenylenedipyrrolidine (IIIa), the structure of which was checked by synthesis from *p*-phenylenediamine and 1,4-dichlorobutane. It was also possible to prepare 1,1'-*p*-phenylenedipiperidine (IIIb) from 1,4-cyclohexanedione and piperidine by the air-oxidation of the bis-enamine intermediate IIb.



II III
(a, x = 1; b, x = 2)

EXPERIMENTAL

Reaction of 1,4-cyclohexanedione with pyrrolidine. A solution of 11.2 g. (0.1 mole) of 1,4-cyclohexanedione in 250 ml. of thiophene-free benzene, to which 28.4 g. (0.4 mole) of pyrrolidine had been added, was heated under reflux in a nitrogen atmosphere for one hour, during which time the theoretical amount of water (3.6 ml.) was collected in a Dean-Stark trap. Evaporation of the benzene in a vacuum yielded 17.5 g. (80%) of a dark red solid, which on sublimation became colorless, m.p. *ca.* 137° (dec.), and remained so on recrystallization from ether at Dry-Ice temperature, m.p. *ca.* 144° (dec.). The analysis was slightly low in carbon and hydrogen for $C_{14}H_{22}N_2$, and the compound appeared to pick up oxygen very rapidly, with coloration. The ultraviolet absorption spectrum in hexane solution exhibited maxima at 272 mμ (log ϵ 4.18), 268 mμ (log ϵ 4.15), and 340 mμ (log ϵ 3.39). The infrared spectrum showed a peak at 1633 and two near 800 cm.$^{-1}$ in addition to those present in the aromatized structure (see below).

Aromatization was effected by bubbling dry air through a benzene solution of the crude diene at 25° for 18 hours. Evaporation of the solvent was followed by sublimation of the product as colorless needles, m.p. 148–150° (dec.); λ_{max}^{hexane} 270 mμ, log ϵ 4.46; 267 mμ, log ϵ 4.42; and 340 mμ, log ϵ 3.62.[4] The infrared spectrum in Nujol was clear above 3060 cm.$^{-1}$ and showed maxima (selected) at 1593 (w), 1531 (s), 1487 (~) and 1470 (s) cm.$^{-1}$. From 1.0 g. of crude bis-enamine IIa there was obtained 0.5 g. of 1,1'-*p*-phenylenedipyrrolidine.

Anal. Calc'd for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.56; H, 9.17; N, 13.23.

The *dipicrate* crystallized as yellow needles from absolute ethanol, m.p. 147–147.5° (dec.).

Anal. Calc'd for $C_{26}H_{26}N_8O_{14}$: C, 46.29; H, 3.89; N, 16.61. Found: C, 46.38; H, 3.83; N, 16.76.

1,1'-p-Phenylenedipyrrolidine from p-phenylenediamine. A mixture of 20 g. (0.16 mole) of 1,4-dichlorobutane, 5.5 g. (0.05 mole) of *p*-phenylenediamine, and 0.5 g. of anhydrous zinc chloride was heated under reflux for 4 hours. Treatment with excess 10% aqueous ammonium hydroxide followed by separation and evaporation of the organic layer yielded 1.0 g. (9%) of crude 1,1'-*p*-phenylenedipyrrolidine. Sublimation gave pure material with the same physical constants as those for the product described above. The melting point of mixtures of 1,1'-*p*-phenylenedipyrrolidine from the two sources was not depressed. Mixtures of the corresponding dipicrates were likewise undepressed in melting point.

Reaction of 1,4-cyclohexanedione with piperidine. A solution of 2.3 g. (0.02 mole) of 1,4-cyclohexanedione and 6.8 g. (0.08 mole) of piperidine in 50 ml. of benzene was heated under reflux in a nitrogen atmosphere for 5 hours. About 0.4 ml. (55%) of water was collected. Evaporation of the benzene yielded a red oil which solidified on cooling. The ether-soluble portion of the residue was sublimed, giving 1.0 g. (22%) of colorless needles, m.p. 142–144° (dec.) (analysis slightly low in carbon and hydrogen for $C_{16}H_{26}N_2$). Aromatization was effected in 57% yield from the crude bis-enamine IIb by air-oxidation. The pure 1,1'-*p*-phenylenedipiperidine was obtained by sublimation as colorless needles, m.p. 108–109°.

Anal. Calc'd for $C_{16}H_{24}N_2$: C, 78.63; H, 9.90; N, 11.47. Found: C, 78.34; H, 9.64; N, 11.52.

The *dipicrate* crystallized as yellow plates from absolute ethanol, m.p. 192–192.5° (dec.).

Anal. Calc'd for $C_{28}H_{30}N_8O_{14}$: C, 47.86; H, 4.30. Found: C, 48.04; H, 4.38.

1,1'-p-Phenylenedipiperidine from p-phenylenediamine. A mixture of 2.3 g. (0.022 mole) of *p*-phenylenediamine, 10.3 g. (0.045 mole) of pentamethylene dibromide, 4.77 g. (0.045 mole) of anhydrous sodium carbonate, and 50 ml. of dry toluene was heated under reflux for 21 hours. Strong aqueous sodium hydroxide was added to the solid phase, and the mixture was extracted with three 50-ml. portions of toluene. The combined toluene extracts were evaporated, giving 3.0 g. of brown powder. The ether-soluble portion yielded about 0.3 g. (6%) of sublimate, m.p. 108–109°, identical with the product described above. The dipicrates were also identical by the usual criteria.

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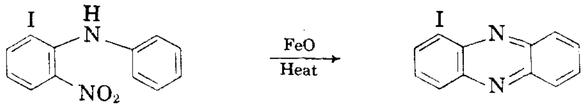
[4] P. Grammaticakis, *Bull. soc. chim. France*, 534 (1951) reported λ_{max}^{EtOH} 263 mμ, log ϵ 4.16, and 312 mμ, log ϵ 3.16, for N,N,N',N'-tetramethyl-*p*-phenylenediamine.

Phenazine Syntheses. IX.[1]
1-Halogenophenazines

Donald L. Vivian

Received May 31, 1956

In the course of extending ring closure through the nitro group[2] to a number of representative phenazines, 1-bromo- and 1-iodophenazine and several alkoxy derivatives of these have been prepared. The syntheses were all made through the 6-halogeno-2-nitrodiphenylamines, as shown by the example:



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[1] Paper VIII, *J. Org. Chem.*, **21**, 1030 (1956).

[2] Waterman and Vivian, *J. Org. Chem.*, **14**, 289 (1949).

With the inclusion of the results given herein, seven of the eight possible 1- and 2-halogenophenazines now are known;[3] only 1-fluorophenazine has not as yet been described.

EXPERIMENTAL

1-Bromophenazine. (*a*). *1-Bromo-2,3-dinitrobenzene.* While this compound has been described both by Wender[4] and by van Duin and van Lennep,[5] it is felt that a more detailed account of the preparation should be given. A solution of 18.3 g. of 2,3-dinitroaniline[6] in 200 cc. of glacial acetic acid was added dropwise to a stirred and cooled solution of 7.7 g. of $NaNO_2$ in 55 cc. of conc'd H_2SO_4, the temperature being held at 15–20°. The resulting diazonium solution then was added over a five-minute period to a stirred solution of 15 g. of Cu_2Br_2, 80 cc. of 48% HBr, and 80 cc. of water, which was maintained at 70–80° during the addition. The cooled solution then was poured into about 2 l. of water, and the precipitate was washed free of acid, giving a quantitative yield of 24.7 g. of 1-bromo-2,3-dinitrobenzene, shrinking at 99°, and melting at 101–102.5°;[7] lit.,[4] m.p. 101.5°. Recrystallized from alcohol, this product melted at 102.5–103.5°.

(*b*). *6-Bromo-2-nitrodiphenylamine.* A mixture of 18.5 g. of 1-bromo-2,3-dinitrobenzene and 26.5 cc. of aniline was refluxed in 375 cc. of absolute ethanol for a period of 3 weeks, and all unchanged material then was removed by steam-distillation. The residue was extracted with ether, the ether was evaporated, and the product was chromatographed on alumina from a benzene solution. Extraction from the alumina by benzene gave 13.2 g. of a very hard, dark red solid melting at 50–52°. Two crystallizations from absolute ethanol gave cinnamon-red microcrystals, m.p. 64–65°.

Anal.[8] Calc'd for $C_{12}H_9BrN_2O_2$: C, 49.2; H, 3.09. Found: C, 49.2; H, 3.24.

(*c*). *1-Bromophenazine.* A mixture of 2.0 g. of 6-bromo-2-nitrodiphenylamine, 2.6 g. of ferrous oxalate dihydrate, and 20 g. of granulated lead in an open flask was heated for 6 minutes in an oil-bath at 267–270°. Sublimation from the broken-up reaction mixture at 270° and about 0.5 mm. gave 1.26 g. of yellow product melting at 126–130°, after earlier softening. Recrystallized twice from *n*-hexane, the compound formed small sulfur-yellow needles, m.p. 132–134°.

Anal. Calc'd for $C_{12}H_7BrN_2$: C, 55.6; H, 2.72. Found: C, 55.9; H, 2.85.

1-Iodophenazine. (*a*). *2,3-Dinitro-1-iodobenzene.* This compound is described by Wender[4] as melting at 138°; as in the case of the bromo compound, it is felt that more details of the method of preparation will be helpful. A diazotization of 18.3 g. of 2,3-dinitroaniline was carried out as given above, and the diazonium solution was added over a period of about 5 minutes to a mechanically-stirred solution of 17 g. of KI in 180 cc. of water, maintained at about 70°. Pouring the resulting solution into an excess of water, filtering, and washing the product free of acetic acid, followed by air-drying, gave 23.3 g. (79%) of crude 1-iodo-2,3-dinitrobenzene, melting at 133–137°. Recrystallization from absolute ethanol (cooling to −50°) gave a product with m.p. 138–140°.

(*b*). *6-Iodo-2-nitrodiphenylamine.* This compound was prepared by refluxing 11.8 g. of 2,3-dinitro-1-iodobenzene and 10.5 cc. of aniline in 215 cc. of absolute ethanol for 8 days. Steam-distillation left a residue which was taken up in hot alcohol, treated with carbon (Darco), and filtered, giving 13.5 g. of a crude red solid. This on recrystallization from ethanol gave orange plates, m.p. 73–75°.

Anal. Calc'd for $C_{12}H_9IN_2O_2$: C, 42.4; H, 2.67. Found: C, 42.4; H, 2.90.

(*c*). *1-Iodophenazine.* A mixture of 1.0 g. of 6-iodo-2-nitrodiphenylamine, 1.3 g. of ferrous oxalate dihydrate, and 10 g. of granulated lead was heated in an open flask in an oil-bath at 268–270° for 7 minutes. On sublimation from the ground mixture at 270° and about 0.5 mm., there was obtained 0.48 g. of crude product. Recrystallized from 3 cc. of chloroform, 0.23 g. of the compound was obtained as short, medium yellow rods, m.p. 142–144°.

Anal. Calc'd for $C_{12}H_7IN_2$: C, 47.1; H, 2.30. Found: C, 47.0; H, 2.54.

1-Bromo-7-methoxyphenazine. (*a*). *6-Bromo-4′-methoxy-2-nitrodiphenylamine.* A mixture of 12.4 g. of 1-bromo-2,3-dinitrobenzene, 18.5 g. of *p*-anisidine, and 250 cc. of absolute ethanol was refluxed for four weeks. The mixture then was poured, with stirring, into a solution of 100 cc. of HCl in 400 cc. of H_2O, the resultant mixture extracted twice with ether, and the ether washed to neutrality. The black, semi-liquid residue from evaporation of the ether was dissolved in benzene and chromatographed on alumina. Elution with benzene and evaporation of the solvent gave a liquid which soon solidified (on scratching) to 13.7 g. of a dull red solid. Two crystallizations from ethanol gave dull red microcrystals, m.p. 65–67°.

Anal. Calc'd for $C_{13}H_{11}BrN_2O_3$: C, 48.3; H, 3.43. Found: C, 48.2; H, 3.70.

(*b*). *1-Bromo-7-methoxyphenazine.* A mixture of 4.0 g. of 6-bromo-4′-methoxy-2-nitrodiphenylamine, 5.2 g. of ferrous oxalate dihydrate, and 40 g. of granulated lead heated for 9 minutes in an oil-bath at 270° (internal temperature reached a maximum of 281°) gave 2.6 g. of yellow product on vacuum-sublimation at about 0.5 mm. from a bath at 270°. Recrystallized twice from benzene, this formed small, pale yellow needles, m.p. 170.5–171°.

Anal. Calc'd for $C_{13}H_9BrN_2O$: C, 54.0; H, 3.14. Found: C, 54.0; H, 3.20.

1-Iodo-7-methoxyphenazine. (*a*). *6-Iodo-4′-methoxy-2-nitrodiphenylamine.* This substance was prepared similarly to the bromo compound, from 14.7 g. of 1,2-dinitro-3-iodobenzene and 18.5 g. of *p*-anisidine, refluxed 4 weeks in 250 cc. of absolute ethanol. The yield was 12.0 g. of a dark red solid, after chromatography. Three recrystallizations from absolute ethanol gave dull red microcrystals, m.p. 79.5–81.5°.

Anal. Calc'd for $C_{13}H_{11}IN_2O_3$: I, 34.3. Found: I, 34.0.

(*b*). *1-Iodo-7-methoxyphenazine.* The size of the reaction flask made considerable difference in the yield obtained from ring closure on the above intermediate. When 2.0 g. of 6-iodo-4′-methoxy-2-nitrodiphenylamine was mixed with 2.6 g. of ferrous oxalate dihydrate and 20 g. of granulated lead in a 10-cc. Erlenmeyer flask, and heated for 8 minutes in a bath at 275–278°, vacuum-sublimation from the mixture gave 0.93 g. of yellow product. Repeated, but in a 25-cc. Erlenmeyer, the yield was only 0.55 g., and the product was much more strongly colored. Recrystallized twice from benzene, the compound forms light yellow small needles or prisms, m.p. 178–180.5°.

Anal. Calc'd for $C_{13}H_9IN_2O$: C, 46.4; H, 2.70. Found: C, 46.5; H, 3.05.

1-Bromo-7-ethoxyphenazine. (*a*). *6-Bromo-4′-ethoxy-2-nitrodiphenylamine.* This compound was prepared similarly to the methoxy homolog. From 9.9 g. of 1-bromo-2,3-dinitrobenzene, there was obtained 9.6 g. of dark red material, which was purified by further chromatography on alumina from benzene solution. In this manner were obtained dark purplish-red microcrystals, m.p. 81–82°.

Anal. Calc'd for $C_{14}H_{13}BrN_2O_3$: C, 49.9; H, 3.88. Found: C, 50.5; H, 3.96.

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(3) Vivian and Hartwell, *J. Org. Chem.*, **18**, 1065 (1953).

(4) Wender, *Gazz. chim. ital.*, **19**, 230 (1889).

(5) van Duin and van Lennep, *Rec. trav. chim.*, **38**, 364 (1919).

(6) Vivian, Hartwell, and Waterman, *J. Org. Chem.*, **20**, 800 (1955).

(7) All melting points given by the author are corrected.

(8) Microanalyses by the Microanalytical Laboratories of the National Institutes of Health, under the direction of Dr. W. C. Alford.

(*b*). *1-Bromo-7-ethoxyphenazine.* When 1.0 g. of 6-bromo-4′-ethoxy-2-nitrodiphenylamine was mixed with 1.3 g. of ferrous oxalate dihydrate and 10 g. of granulated lead, heating the mixture for 12 minutes in a bath at 255–260° gave 0.63 g. product on vacuum-sublimation from the whole ground sublimation mixture at 270° and about 0.5 mm. This product had a good deal of red material in it, however, so it was again subjected to treatment with ferrous oxalate dihydrate and granulated lead, as before, giving 0.50 g. of light-yellow microcrystals, m.p. 156–157°, on purification by vacuum-sublimation at about 0.5 mm., from a bath at 270°.

Anal. Calc'd for $C_{14}H_{11}BrN_2O$: C, 55.5; H, 3.66. Found: C, 55.9; H, 3.80.

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Ethyl 4-Formylphenoxyacetate

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The preparation of ethyl 4-formylphenoxyacetate (I) from 4-formylphenoxyacetic acid and ethyl alcohol has been reported.[1] The product was impure, disintegrating at 100° and becoming completely liquid at 155°.

We wish to report the preparation of I from *p*-hydroxybenzaldehyde and ethyl bromoacetate using the potassium carbonate method employed by A. Robertson[2] for the *ortho* isomer. Our product, after recrystallization, melted at 42–42.5° and the analyses for it and the oxime derivative were consistent with the values calculated for I and its oxime. The infrared spectrum of the product indicated the presence of ester, arylaldehyde, and phenoxy groupings and *para* substitution.

We submit this evidence in correction of the prior literature on the compound I.

EXPERIMENTAL

Ethyl 4-formylphenoxyacetate (I). Ethyl bromoacetate (167 g.), *p*-hydroxybenzaldehyde (122 g.), potassium carbonate (138 g.), and dry acetone (500 ml.) were stirred vigorously under reflux conditions for two hours. The mixture then was poured, with stirring, into two liters of ice-water. The resulting solid was filtered, washed well with ice-water and dried (1) by pressing with a rubber dam and (2) over calcium chloride in a vacuum desiccator.

The light yellow product melted at 35–38° and amounted to 175 g. (84.1%). One crystallization from ethanol raised the m.p. to a constant 42–42.5° (uncorr.).

Anal. Calc'd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.53; H, 5.59.

Oxime. The oxime was prepared according to method A in Shriner and Fuson, *Identification of Organic Compounds*, Second Edition, John Wiley and Sons, New York, N. Y., 1940, page 167. The oxime (white needles from alcohol-water) melted at 61–62° (uncorr.).

Anal. Calc'd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87. Found: C, 58.81; H, 5.60.

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[1] Elkan, *Ber.*, 19, 3042 (1886).

[2] Robertson, *J. Chem. Soc.*, 489 (1933).

The Chlorination of Phenyldimethylsilane[1]

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Received June 4, 1956

It has been shown that at 80° the relative reactivities of the α- and β-hydrogen atoms of cumene towards a chlorine atom are 12.8:1.[2] It would be of interest if similar data on the reactivities of the hydrogen atoms of the silicon analog of cumene, phenyldimethylsilane, were available. Since silicon-hydrogen bonds usually are weaker than carbon-hydrogen bonds,[3] it is expected that generally a chlorine atom will react with a silicon-hydrogen bond in preference to a carbon-hydrogen bond. In the case of cumene and its silicon analog this generality may not apply since the 2-phenyl-2-propyl radical undoubtedly possesses considerably more resonance stabilization than the phenyldimethylsilyl radical.[4] In fact, towards the highly selective peroxy radical the α-hydrogen atom of cumene is about 200 times as reactive as the α-hydrogen atom of phenyldimethylsilane, presumably because of this resonance effect.[5]

When phenyldimethylsilane was photochemically chlorinated in the liquid phase at 80° we observed that substitution at the α-position occurred 30 times as readily as substitution at the β-position. However, further investigation demonstrated that the substitution reaction occurred as readily in the dark as in the presence of intense illumination. Apparently an ionic substitution reaction occurred so readily that the free radical reaction was completely overshadowed. The cleavage of silicon-hydrogen bonds by bromine in the dark has been observed previously.[6] Presumably ionic substitution by chlorine occurs in a similar manner involving

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[1] Directive Effects in Aliphatic Substitutions. VIII.

[2] G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4031 (1955).

[3] Unfortunately, bond dissociation energies for various silicon-hydrogen bonds are not available. The silicon-hydrogen bond strength of silane (80.8 kcal. mole^{-1}) is 10 kcal. mole^{-1} less than the carbon-hydrogen bond energy of methane (90.8 kcal. mole^{-1}) [M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953)].

[4] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

[5] G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

[6] A. Stock and C. Somieski, *Ber.*, **50**, 1739 (1917); C. Eaborn, *J. Chem. Soc.*, 2755 (1949); W. H. Nebergall and O. H. Johnson, *J. Am. Chem. Soc.*, **71**, 4022 (1949); W. H. Nebergall, *J. Am. Chem. Soc.*, **72**, 4702 (1950).