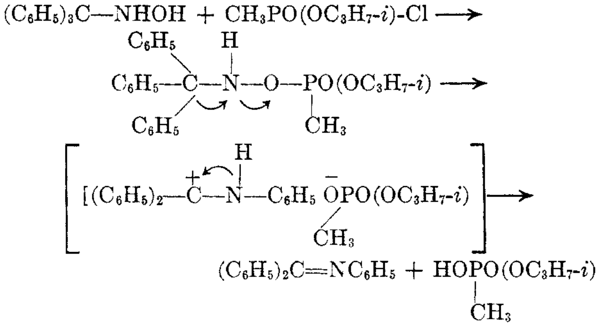
ing unstable phosphorylated product is believed to undergo a concerted change involving loss of phosphonic acid and the simultaneous migration of a phenyl group from carbon to nitrogen.



An initial phosphorylation on the nitrogen rather than on the oxygen of the triphenylmethylhydroxylamine molecule followed by loss of phosphonic acid could also yield the same product.

Triphenylmethylhydroxylamine, when treated with diisopropyl phosphorochloridate under the same conditions as isopropyl methylphosphonochloridate, did not react.

EXPERIMENTAL

Reaction of amidoximes with Sarin, DFP, and the corresponding chloro analogs. The amidoxime[6] was dissolved in the minimum amount of water and the solution was adjusted to *p*H 7.6. An equimolar amount of the fluorophosphate or the fluorophosphonate was added to this solution with stirring and a constant *p*H 7.6 was maintained by titration with alkali from a Beckmann Model K autotitrimeter. When the reaction was completed, the solution was made acid and the product was isolated by filtration or by extraction of the acidic solution with chloroform or ether. Recrystallization from appropriate solvents yielded the phosphonylated products.

The same products could be obtained by reacting 1 mole of amidoxime with 1 mole of chlorophosphate or chlorophosphonate in a non-aqueous solvent in the presence of triethylamine. Several of the phosphorylated products were first isolated only as oils but were obtained crystalline after passage over a column of activated alumnia prior to recrystallization.

The physical and analytical data for the phosphorylated amidoximes are contained in Table I.

Preparation of N,N-dimethylbenzamidoxime. To a stirred solution of benzohydroximyl chloride (15.5 g., 0.1 mole) dissolved in 30 cc. of absolute alcohol maintained at 0° was added 50 cc. of a solution of dimethylamine, (9.9 g., 2.2 moles) in absolute alcohol. The mixture was kept at 0° for 30 minutes and then was allowed to stir at room temperature in a stoppered filtering flask for 24 hours. Part of the alcohol was removed *in vacuo.* Cooling yielded a solid which was filtered and washed with cold alcohol. On recrystallization from alcohol the solid melted at 120°.

Anal. Calc'd for $C_9H_{12}N_2O$: C, 66.0, H, 7.3. Found: C, 66.0, H, 7.4.

This material was reacted with the chloro derivative of Sarin (Table I).

Rearrangement of Sarin-phosphorylated benzamidoxime to phenylurea. Sarin-phosphorylated benzamidoxime (4.0 g.) was placed in 15 cc. of water and was refluxed for 1 hour. After separating the water solution from an oily material and cooling, 150 mg. of a solid was obtained melting at 147° whose analysis corresponded to that of phenylurea.

Anal. Calc'd for $C_7H_8N_2O$: C, 61.8, H, 5.90, N, 20.6. Found: C, 62.0, H, 5.8, N, 20.7.

The reddish-brown oil which also formed was not identified.

Rearrangement of triphenylmethylhydroxylamine to benzophenone anil. Isopropyl methylphosphonochloridate (1.57 g., 0.01 mole) was added dropwise to a stirred, cooled solution of triphenylmethylhydroxylamine (2.75 g., 0.01 mole) in benzene in the presence of triethylamine (1.01 g., 0.01 mole). The mixture then was allowed to come to room temperature and was kept at room temperature for two hours. The amine hydrochloride was filtered and the solution was concentrated to dryness. The residue was crystallized from absolute alcohol and yielded 1.2 g. of a solid of m.p. 111°. This solid did not contain phosphorus and gave a negative Tollens test. Elemental analysis conformed with that of benzophenone anil.

Anal. Calc'd for $C_{19}H_{15}N$: C, 88.5, H, 5.85, N, 5.43. Found: C, 88.3, H, 5.80, N, 5.10.

In order to prove that the substance of m.p. 111° was the anil, 0.2 g. was hydrolyzed with 18% hydrochloric acid to benzophenone and aniline. The former was isolated as its 2,4-dinitrophenylhydrazone, the latter as its benzenesulfonanilide. Mixture melting point determination with authentic samples of these derivatives gave no depression.

Triphenylmethylhydroxylamine when treated with diisopropyl phosphorochloridate under the same conditions as isopropyl methylphosphonochloridate did not react.

Acknowledgment. The authors wish to thank the Analytical Research Branch of the Research Directorate, Chemical Warfare Laboratories for performing the analytical determinations.

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Unsaturated Amines. IX. Through Bis-Enamines to Aromatics[1]

Nelson J. Leonard and Ronald R. Sauers[2]

Received May 31, 1956

The preparation of enamines[3] by the reaction of ketones with piperidine and pyrrolidine suggested an application to the synthesis of substituted *p*-phenylenediamines from 1,4-cyclohexanedione. The heating of a mixture of 1,4-cyclohexanedione (I) and pyrrolidine, with collection of the theoretical amount of water, gave a product exhibiting the in-

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[6] Acetamidoxime: Michaelis, *Ber.*, **24**, 3439 (1891); Benzamidoxime: Krüger, *Ber.*, **18**, 1053 (1885); Nicotinamidoxime: Nordmann, *Ber.*, **17**, 2746 (1884).

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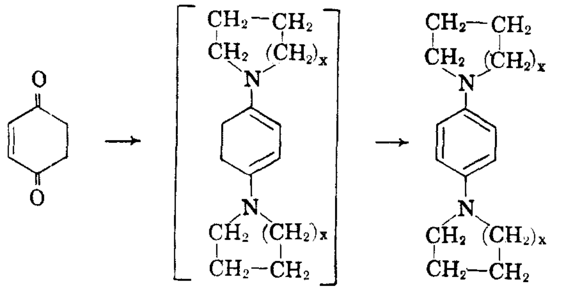
(1) Article VIII in this series: N. J. Leonard, L. A. Miller, and P. D. Thomas, *J. Am. Chem. Soc.*, **78**, 3463 (1956).

(2) National Science Foundation Fellow, 1954–1955.

(3) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936); F. W. Heyl and M. E. Herr, *J. Am. Chem. Soc.*, **75**, 1918 (1953); M. E. Herr and F. W. Heyl, *J. Am. Chem. Soc.*, **75**, 5927 (1953); G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954); J. L. Johnson, M. E. Herr, J. C. Babcock, R. P. Holysz, A. E. Fonken, J. E. Stafford, and F. W. Heyl, *J. Am. Chem. Soc.*, **78**, 430 (1956).

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

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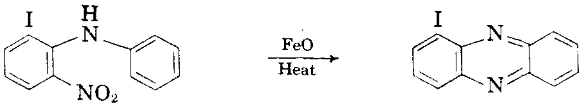
In the course of extending ring closure through the nitro group[2] to a number of representative phenazines, 1-bromo- and 1-iodophenazine and several alkoxy derivatives of these have been prepared. The syntheses were all made through the 6-halogeno-2-nitrodiphenylamines, as shown by the example:



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

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