2.4 g. of diethyl phosphite and heated for 8 hr. at 100°. The reaction mixture yielded 1.4 g. (31%) of diethyl β-phenylethyl-α-aminophosphonate hydrochloride, which formed colorless needles, m.p. 230–232°, after crystallization from water.

Anal. Calcd. for $C_{12}H_{21}O_3NPCl$: P, 10.56; N, 4.77; Cl, 11.89. Found: P, 10.42; N, 4.46; Cl, 11.93.

The ester was hydrolyzed and the free amino acid was isolated by the aniline method. The acid, obtained in 83% yield, formed cross-shaped crystals which melted at 225–227°.

Anal. Calcd. for $C_8H_{12}O_3NP$: P, 15.42; N, 6.97. Found: P, 15.50; N, 7.06.

Aminomethylphosphonic Acid.—This compound was prepared according to Chavanne[6] in order that a more convenient method of isolation be explored.

Bromomethylphthalimide (100 g.) and 54.6 g. of triethyl phosphite were heated at 150–160° until the evolution of ethyl bromide ceased. The residue was refluxed for 12 hr. with 100 ml. of 48% hydrobromic acid and phthalic acid was filtered from the cooled solution. The filtrate was evaporated to dryness, taken up in 100 ml. of dry ethanol and the clear solution treated with aniline until it became slightly acid to congo red. The precipitated acid was taken up in water, neutralized with sodium hydroxide and steam-distilled to remove traces of aniline. The solution was acidified to litmus with hydrochloric acid and treated with a saturated solution of lead acetate. The precipitate was thoroughly washed with hot water and the suspension was treated with hydrogen sulfide. Evaporation of the filtrate and recrystallization of the resulting crude acid from water gave a 58% yield of pure aminomethylphosphonic acid, m.p. above 300°.

Anal. Calcd. for CH_6O_3NP: P, 27.92; N, 12.61. Found: P, 28.10; N, 12.74.

The Mannich reaction with dialkylamines and dialkyl phosphites has been also reported by Fields.[7] Two products of this reaction that were necessary for our studies were prepared in good yield by the procedure given by Fields. Since Fields does not cite any physical properties of his products other than boiling points, the following may be of interest: diethyl N,N-diethylaminomethylphosphonate, b.p. 128–130° at 15 mm., $n^{20}D$ 1.3848, d^{20}_4 0.8779; diethyl α-(N,N-diethylamino)-isopropylphosphonate, b.p. 94–95° at 15 mm., $n^{20}D$ 1.4190, d^{20}_4 0.9256.

(6) V. Chavanne, *Bull. soc. chim., France*, **15**, 774 (1948).

(7) E. K. Fields, THIS JOURNAL, **74**, 1528 (1952).

AUBURN, ALA.

[CONTRIBUTION FROM ABBOTT LABORATORIES]

The Reaction of 1,5-Dibromopentane with *o*-Substituted Anilines. The Synthesis of 1-Arylpiperidines[1]

BY ARMIGER H. SOMMERS AND SHARON E. AALAND

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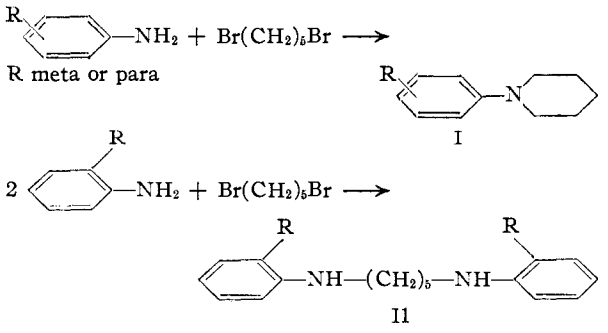
The reaction of *o*-toluidine, *o*-anisidine, *o*-chloroaniline or α-naphthylamine with 1,5-dibromopentane yielded an N-(*o*-substituted-phenyl)-piperidine (IV) as the principal product, although a small amount of an N,N'-diarylpentamethylenediamine (II) was sometimes isolated as by-product. 2,6-Dimethoxyaniline behaved similarly; however, the only product obtained with 2,6-dimethylaniline is N,N'-bis-(2,6-dimethylphenyl)-pentamethylenediamine (VII), a result which indicates greater steric hindrance by the two methyl groups. *m*-Anisidine gave N-*m*-methoxyphenylpiperidine from this reaction, and demethylation of the methoxyphenylpiperidines provided the corresponding aminophenols. Two of these were converted to dimethylcarbamyl esters, and quaternary salts were prepared and tested as anti-curare agents.

Soon after von Braun described a synthesis of 1,5-dibromopentane[2] this compound was used by Scholtz and Wassermann[3] for the synthesis of *m*- or *p*-substituted N-phenylpiperidines (I) from the corresponding substituted anilines. An *o*-substituent, they reported, prevented the formation of a piperidine ring and led to the formation of an N,N'-diarylpentamethylenediamine (II).



This conclusion was accepted by von Braun[4] and reference to it is made, without comment, in more recent publications,[5] but there seems to be no other experimental evidence to indicate that sufficient steric hindrance exists in *o*-substituted anilines to prevent N,N-disubstitution. To the contrary, two papers[6,7] take exception to physical data presented for N-tolylpiperidines prepared by this reaction, and other results have been reported which are not compatible with those of Scholtz and Wassermann.[3] Cerkovnikov and Prelog[8] obtained N-arylpiperidines by the action of 3-dimethylamino-1,5-dibromopentane upon *o*-toluidine and α-naphthylamine. This cannot be reconciled with the failure of 1,5-dibromopentane to undergo similar ring formation, unless the reactions are significantly different. A possible intermediate[9] in the former alkylation is 1,1-dimethyl-2-(β-bromoethyl)-azetidinium bromide, which was prepared by Cerkovnikov and Prelog,[8] and which yields a substituted piperidine upon treatment with aniline. These authors con-

(1) Presented before the Organic Division of the American Chemical Society, Chicago, Ill., September, 1953.

(2) J. von Braun, *Ber.*, **37**, 3210 (1904).

(3) M. Scholtz and E. Wassermaun, *ibid.*, **40**, 852 (1907).

(4) J. von Braun, *ibid.*, **41**, 2156 (1908).

(5) J. Houben, "Die Methoden der Organischen Chemie," Third Edition, Vol. 4, George Thieme, Leipzig, 1941, (Edwards Brothers, Inc., Ann Arbor, Mich., 1944), p. 580; A. A. Morton, "The Chemistry of Heterocyclic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 232.

(6) A. N. Bourns, H. W. Embleton and M. K. Hansuld, *Can. J. Chem.*, **30**, 1 (1952).

(7) J. von Braun, *Ber.*, **40**, 3922 (1907).

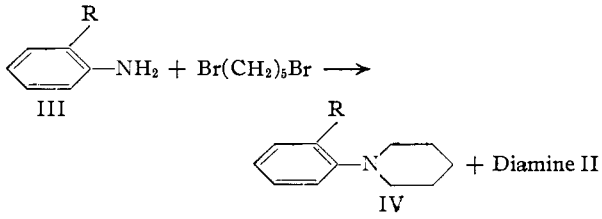
(8) E. Cerkovnikov and V. Prelog, *ibid.*, **74**, 1648 (1941).

(9) R. C. Elderfield and C. Ressler, THIS JOURNAL, **72**, 4059 (1950).

cluded, however, that the alkylating agent here is the original open chain bromide rather than the substituted azetidinium ion.

Bourns, Embleton and Hansuld[6] prepared the three isomeric N-tolylpiperidines by the vapor phase reaction of the appropriate toluidine with tetrahydropyran over alumina. The yield of N-(*o*-tolyl)-piperidine was good, though somewhat lower than the yields of the isomeric compounds. Hünig[10] reported the preparation of N,N-dimethyl-*o*-toluidine and N,N-dimethyl-α-naphthylamine by methylation of the primary amines with dimethyl sulfate. Here again the yields of tertiary amines were good, in spite of some evidence of steric hindrance.

We have carried out the reaction of 1,5-dibromopentane with three *o*-monosubstituted anilines (III, R = CH_3, OCH_3, Cl) and with α-naphthylamine, and in every case obtained the corresponding N-arylpiperidine IV as the principal product.

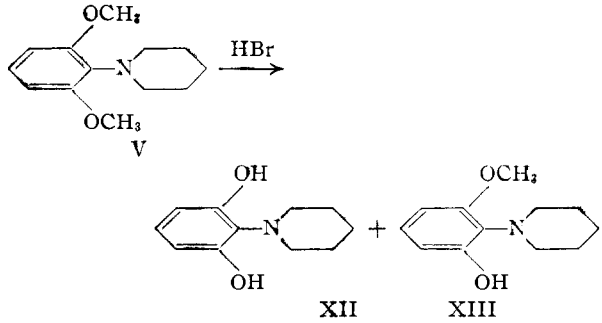


m-Anisidine in like manner yielded N-(*m*-methoxyphenyl)-piperidine. No identifiable product was isolated from the reaction when *o*-nitroaniline was used. Our results with this amine may be attributed to its comparatively low basicity,[10,11] and the same reason may account for the fact, noted also by others,[3] that *o*-chloroaniline requires a higher temperature for reaction with 1,5-dibromopentane than does *o*-toluidine or *o*-anisidine. The N-arylpiperidines are described together with their salts in Table I.

In addition to the piperidines, low yields of N,N'-disubstituted pentamethylenediamines (II) were obtained from *o*-toluidine and *o*-anisidine in this reaction. A similar mixture of products, N-(2,6-dimethoxyphenyl)-piperidine (V) and N,N'-bis-(2,6 - dimethoxyphenyl) - pentamethylenediamine (VI), was obtained when 2,6-dimethoxyaniline and 1,5-dibromopentane were heated together. 2,6-Dimethylaniline, however, yielded only the open chain compound, N,N'-bis-(2,6-dimethylphenyl)-pentamethylenediamine (VII). The melting points of the diamines differ from those given by Scholtz and Wassermann for these compounds.[3]

The difference observed in the behavior of 2,6-dimethylaniline, in which both *o*-positions are occupied, and that of *o*-toluidine is in conformity with other reactions of these amines[12] and of related compounds.[13,14] It is evident that two *o*-methyl groups are more effective than two *o*-methoxy groups in shielding an amine,[14] while a single methyl, methoxy or chloro *o*-substituent is not able to prevent disubstitution by the pentamethylene radical.

Demethylation of N-(*o*-methoxyphenyl)-piperidine yielded the phenol VIII, which on treatment with N,N-dimethylcarbamyl chloride gave the ester X. Quaternary salts (IX and XI) of these bases were prepared and the same series of reactions was carried out on N-(*m*-methoxyphenyl)-piperidine. A mixture of N-(2,6-dihydroxyphenyl)-piperidine (XII) and N-(2-hydroxy-6-methoxyphenyl)-piperidine (XIII) was obtained from the reaction of N-(2,6-dimethoxyphenyl)-piperidine (V) and hydrobromic acid. The properties of the phenolic piperidines and their derivatives are given in Table II.



One of the quaternary salts, N-(*m*-hydroxyphenyl)-N-methylpiperidinium iodide, is structurally similar to *m*-hydroxyphenyldimethylethylammonium chloride (Tensilon), and has been tested for anti-curare activity by Dr. G. M. Everett and Mr. J. S. Goodsell of these laboratories. They report this drug to be more effective than Tensilon in rabbits and mice if given prior to curare but much less effective than Tensilon when given after curare. The *o*-hydroxy isomer IX is inactive.[15]

Experimental

Substituted Anilines.—With two exceptions these were obtained from Eastman Kodak Co. ***m*-Anisidine** was prepared by Mr. Morris Freifelder and Mr. George Stone of these laboratories by low pressure hydrogenation of *m*-nitroanisole in alcohol over palladized charcoal. The yield of product which boiled at 132° (19 mm.) was 91%.[16] **2,6-Dimethoxyaniline,**[17] m.p. 77–78°, was similarly obtained in the theoretical yield from 2,6-dimethoxynitrobenzene, which was prepared by methylation of 2-nitroresorcinol.[18] **The picrate** was prepared in dry ether; m.p. 169–170°.

Anal. Calcd. for $C_{14}H_{14}O_9$: N, 14.66. Found: N, 14.54.

N-Arylpiperidines (Table I) and Pentamethylenediamines.—Two general procedures (A and B) are exemplified using *o*-toluidine. Deviations from these procedures are noted for specific compounds.

From *o*-Toluidine. Method A.—A mixture of 12 g. (0.11 mole) of *o*-toluidine and 5 g. (0.022 mole) of 1,5-dibromopentane was heated on a steam-bath for 30 minutes. The crystalline mass which formed was stirred with dry ether and the insoluble *o*-toluidine hydrobromide collected. It weighed 8.3 g., the theoretical amount. The filtrate was concentrated and distilled yielding 2.3 g. (60%) of **N-(*o*-tolyl)-piperidine**[6] (IV, R = CH_3), b.p. 65–66° (0.6 mm.), and 0.5 g. (8%) of **N,N'-bis-(*o*-tolyl)-pentamethylenedi-**

(10) S. Hünig, *Ber.*, **85**, 1056 (1952).

(11) R. Adams and N. K. Sundholm, THIS JOURNAL, **70**, 2667 (1948).

(12) R. Lesser, *Ann.*, **402**, 49 (1914); F. Kehrmann, M. Ramm and C. Schmajewski, *Helv. Chim. Acta*, **4**, 538 (1921).

(13) N. Buu-Hoi and P. Cagniant, *Bull. soc. chim. France*, **9**, 727 (1942).

(14) R. C. Fuson, C. H. McKeever, N. Rabjohn and H. W. Gray, THIS JOURNAL, **65**, 1028 (1943).

(15) Personal communication from Dr. G. M. Everett.

(16) P. Grammaticakis, *Bull. soc. chim. France*, 225 (1951).

(17) H. Kauffmann and W. Franck, *Ber.*, **40**, 3999 (1907); T. Ekstrand and N. Löfgren, *Acta Chem. Scand.*, **6**, 1016 (1952).

(18) H. Kauffmann and E. dePay, *Ber.*, **37**, 725 (1904); A. Baeyer, *Ann.*, **372**, 126 (1910); C. B. Jaeger, Jr., U. S. Patent 2,385,282; *C. A.*, **40**, 1883 (1946).

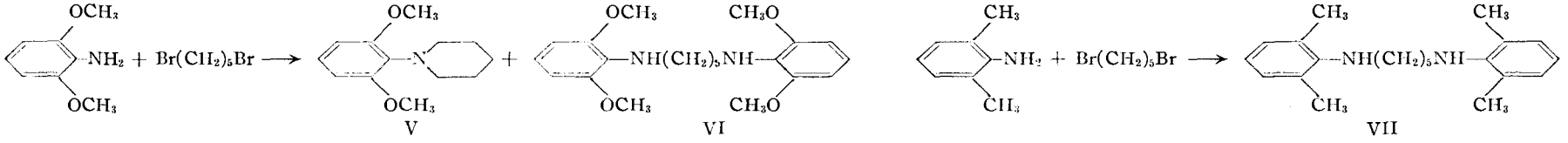


TABLE I

1-ARYLPIPERIDINES AND SALTS Ar—N(CH2—CH2)2CH2

Ar	Method	Yield, %	B.p., °C.	Mm.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrochlorides M.p., °C.	Hydrochlorides Nitrogen, % Calcd.	Hydrochlorides Nitrogen, % Found	Picrates M.p., °C.	Picrates Nitrogen, % Calcd.	Picrates Nitrogen, % Found
o-$CH_3C_6H_4$–[a]	A	60	65–66	0.6	1.5384	$C_{12}H_{17}N$	82.23	82.03	9.78	9.48	7.99	7.79	190–191	6.62	6.81	152–153	13.86	13.87
	B	59																
o-$OCH_3C_6H_4$–	A	60	128	8.0	1.5520	$C_{12}H_{17}NO$	75.35	75.44	8.96	8.85	7.32	7.38	183	6.15	6.28	128–129	13.33	13.67
	B	76																
o-ClC_6H_4–	A[b]	31	125	7.0	1.5610	$C_{11}H_{14}ClN$	67.51	67.25	7.21	7.17	7.16	7.25	174–175	6.03	[c]	136–138	13.19	13.00
m-$OCH_3C_6H_4$–	B	46	89	0.1	1.5609	$C_{12}H_{17}NO$	75.35	75.02	8.96	8.74	7.32	7.19	196–198	6.15	6.06	162–163	13.33	13.50
α-Naphthyl[d]	B	38	143	2.0	1.6185	$C_{15}H_{17}N$	85.26	85.21	8.11	8.16	6.63	6.79	184–186	5.65	5.61	124	12.72	12.91
o,*o*-$DiOCH_3C_6H_3$–	A	45	138–139[e]	7.0	1.5452	$C_{13}H_{19}NO_2$	70.56	70.35	8.65	8.52	6.33	6.64	123–130	5.44	5.49	152–153	12.44	12.45

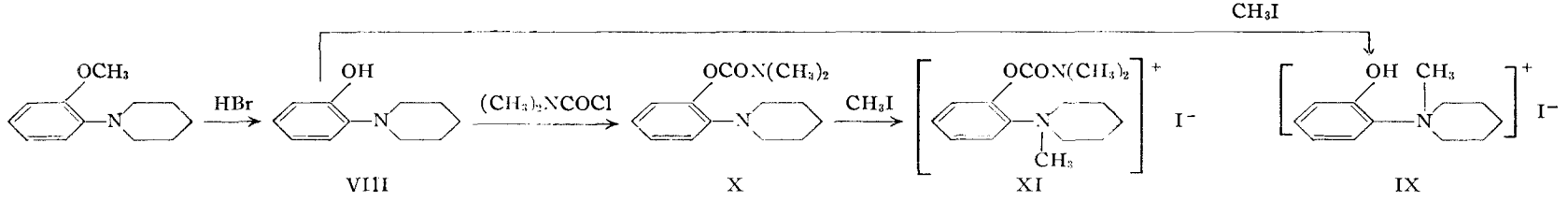
[a] Reference 6 gives b.p. 141.2–141.9° at 28 mm., $n^{25}D$ 1.5392, picrate m.p. 153.8–154.1°. [b] Reaction temperature 120°. [c] This salt gave high values (7 to 8%) for nitrogen, indicating loss of hydrogen chloride. [d] References 19 and 20. [e] M.p. 38.5–39.5°.

TABLE II

PHENOLIC PIPERIDINES, CARBAMATES AND SALTS R—N(CH2—CH2)2CH2

R	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrochlorides M.p., °C.	Hydrochlorides Nitrogen, % Calcd.	Hydrochlorides Nitrogen, % Found	Methiodides M.p., °C.	Methiodides Carbon, % Calcd	Methiodides Carbon, % Found	Methiodides Hydrogen, % Calcd.	Methiodides Hydrogen, % Found
o-OHC_6H_4–	56	70–72	$C_{11}H_{15}NO$	74.54	74.55	8.53	8.36	7.90	8.05	176–178	6.56	6.58	166–167	45.15	45.51	5.68	5.65
m-OHC_6H_4–[a]	81	123–124	$C_{11}H_{15}NO$	74.54	74.58	8.53	8.40	7.90	7.77	218–219[b]	5.43	5.42	138–139	45.15	45.49	5.68	5.76
o-$OOCN(CH_3)_2C_6H_4$–	72	[c]	$C_{14}H_{20}N_2O_2$	67.71	67.80	8.12	8.08	11.28	11.40	145–146	9.84	9.84	131–134	46.16	46.44	5.94	5.96
m-$OOCN(CH_3)_2C_6H_4$–	24	[d]	$C_{14}H_{20}N_2O_2$	67.71	67.72	8.12	8.09	11.28	11.29	200–204	9.84	9.68	131–133	46.16	47.25	5.94	6.01
o,*o*-$Di\text{-}OHC_6H_3$–	35	169–170	$C_{11}H_{15}NO_2$	68.37	68.53	7.82	7.66	7.25	7.15	269–270	6.10	6.22					
o-OH,*o*-$OCH_3C_6H_4$–	40	60–80	$C_{12}H_{17}NO_2$	69.53	69.27	8.27	8.14	6.76	6.74	[e]							

[a] Reference 21. [b] Hydrobromide. [c] B.p. 113–118° (0.1 mm.), $n^{25}D$ 1.5404. [d] B.p. 143–145° (0.1 mm.), $n^{25}D$ 1.5566. [e] No solid salts were obtained.



amine (II, R = CH_3), b.p. 177° (0.1 mm.). The latter was purified by conversion to the **dihydrochloride** salt, m.p. 202–207°.

Anal. Calcd. for $C_{19}H_{28}Cl_2N_2$: N, 7.89. Found: N, 7.70.

This salt was reconverted to the free base, $n^{25}D$ 1.5857.

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92. Found: C, 81.10; H, 9.12; N, 10.10.

This compound, for which Scholtz and Wassermann[3] give m.p. 76–77°, did not solidify.

Method B.—A mixture of 10.7 g. (0.1 mole) of *o*-toluidine, 23 g. (0.1 mole) of 1,5-dibromopentane and 10.6 g. (0.1 mole) of anhydrous sodium carbonate in 30 ml. of dry toluene was stirred while refluxing for 24 hours. The toluene solution was then decanted from a gummy solid which was dissolved in water. The aqueous solution was made strongly basic with sodium hydroxide and shaken with toluene. The combined toluene solutions were concentrated and distilled. Redistillation of the product gave 10.3 g. (59%) of N-(*o*-tolyl)-piperidine.

From *o*-**Anisidine.**—Method A yielded 60% of **N-(*o*-methoxyphenyl)-piperidine** (IV, R = OCH_3) and 9% of **N,N'-bis-(*o*-methoxyphenyl)-pentamethylenediamine** (II, R = OCH_3), boiling at 217° (0.13 mm.). The latter compound was crystallized from ethanol and melted at 91–92°. Scholtz and Wassermann[3] give m.p. 131°.

Anal. Calcd. for $C_{19}H_{26}N_2O_2$: C, 72.58; H, 8.34; N, 8.91. Found: C, 72.45; H, 8.19; N, 8.89.

N,N'-Bis-(*o*-methoxyphenyl)-pentamethylenediamine **dihydrochloride** crystallized as white needles, m.p. 196–198°, in a mixture of ethanol and ether.

Anal. Calcd. for $C_{19}H_{28}Cl_2N_2O_2$: N, 7.23. Found: N, 7.06.

From α-**Naphthylamine.**—Method B gave 38% of **N-(α-naphthyl)-piperidine**, b.p. 143° (2 mm.). This compound has been prepared previously by the condensation of piperidine with α-bromonaphthalene[19] or α-naphthol.[20] Abel[20] describes the **hydrochloride**, m.p. 178–179°, and the **picrate** (for which no analytical data are presented), m.p. 179–180°. We found m.p. 184–186° for the hydrochloride and m.p. 124° for the picrate. Analytical results for these salts are included in Table I.

From **2,6-Dimethoxyaniline.**—A mixture of 16.8 g. (0.11 mole) of 2,6-dimethoxyaniline and 5 g. (0.022 mole) of 1,5-dibromopentane was heated two hours on steam and then shaken with benzene and water. Evaporation of the benzene layer gave 10 g. of recovered 2,6-dimethoxyaniline, m.p. 76–77°. The aqueous layer was basified and the resulting oil was extracted with benzene, concentrated and distilled. Fraction 1, boiling from 120° to 130° (6 mm.), weight 4 g., was recovered 2,6-dimethoxyaniline. Fraction 2, boiling at 130–142° (6 mm.) was redistilled and identified as **N-(2,6-dimethoxyphenyl)-piperidine** (**V**) by analysis of the base and its salts, which are described in Table I. Fraction 3, boiling at 222–223° (0.1 mm.), weight 0.8 g. (10%), $n^{25}D$ 1.5683, remained a light yellow, viscous oil, and was **N,N'-bis-(2,6-dimethoxyphenyl)-pentamethylenediamine** (**VI**).

Anal. Calcd. for $C_{21}H_{30}N_2O_4$: C, 67.35; H, 8.08; N, 7.48. Found: C, 67.66; H, 8.11; N, 7.26.

This base gave an oily hydrochloride salt. The salt obtained with picric acid gave analytical values between those calculated for the mono- and dipicrates.

From **2,6-Dimethylaniline.**—A mixture of 13.4 g. (0.11 mole) of 2,6-dimethylaniline and 5 g. (0.022 mole) of 1,5-dibromopentane was heated for three hours on a steam-bath and the resulting solid was triturated first with 500 ml. of anhydrous ether and then with 75 ml. of hot absolute ethanol. There was obtained 5.1 g. (49%) of the **dihydrobromide** salt, m.p. 248°, of **N,N'-bis-(2,6-dimethylphenyl)-pentamethylenediamine** (**VII**).

Anal. Calcd. for $C_{21}H_{32}Br_2N_2$: C, 53.40; H, 6.83; N, 5.93. Found: C, 53.31; H, 6.98; N, 5.63.

The liberated base boiled from 175 to 180° (0.1 mm.), and soon crystallized. It weighed 3 g. (44%) and melted at 41–42°.

Anal. Calcd. for $C_{21}H_{30}N_2$: C, 81.23; H, 9.74; N, 9.03. Found: C, 81.20; H, 9.70; N, 9.23.

The dihydrochloride salt crystallized from ethanol and melted at 247–248°.

Anal. Calcd. for $C_{21}H_{32}Cl_2N_2$: N, 7.31. Found: N, 7.16.

Scholtz and Wassermann[3] state that the base, which they obtained in the same manner, crystallizes from alcohol and melts at 228°. They present analytical data for this material, $C_{21}H_{30}N_2$, but the physical properties do not agree with those of the compound prepared by us.

N-Hydroxyphenylpiperidines and Derivatives (Table II). **N-(*o*-Hydroxyphenyl)-piperidine.**—A solution of 4.4 g. of N-(*o*-methoxyphenyl)-piperidine in 50 ml. of 48% hydrobromic acid was refluxed for 16 hours. Concentration of the solution gave a brown oil which was dissolved in water and treated with sufficient 10% sodium hydroxide solution to precipitate the free aminophenol as a brown oil which soon crystallized. It was distilled in a sausage flask at 0.1 mm., in a bath at 130°, and formed a light solid, m.p. 70–72°.

N-(*m*-Hydroxyphenyl)-piperidine, similarly prepared, precipitated on the addition of base as pinkish crystals whose melting point, 123–124°, was unchanged after recrystallization fron Skellysolve B. A patent reference[21] to this compound, prepared by the reaction of resorcinol with piperidine at 150°, gives no description of its physical properties.

N-(*o*-Dimethylcarbamyloxyphenyl)-piperidine (**X**).—A solution of 1.5 g. of N-(*o*-hydroxyphenyl)-piperidine and 1.1 g. of dimethylcarbamyl chloride in 25 ml. of dry pyridine was heated on a steam-bath for three hours. The pyridine was removed under vacuum and the residue was treated with 50 ml. of 5% sodium hydroxide solution. The dark oil which separated was extracted with benzene and distilled. **The hydrochloride** salt, oily at first, formed large colorless crystals on standing under dry ether.

N-(*m*-Dimethylcarbamyloxyphenyl)-piperidine, obtained similarly, gave a flocculent yellow **hydrochloride** salt.

Quaternary salts (**IX**, **XI**) were prepared from N-(*o*-hydroxyphenyl)-piperidine and N-(*m*-hydroxyphenyl)-piperidine, and from their dimethylcarbamates, by heating the tertiary amine with methyl iodide in acetone solution. Evaporation of the solvent gave the methiodides, usually as oils which solidified under dry ether. They were crystallized from alcohol–ether or methyl ethyl ketone–ether mixtures.

Acknowledgment.—We thank Mr. E. F. Shelberg, Mr. Robert H. Berg, and other members of the Microanalytical Department for the analytical results reported here.

NORTH CHICAGO, ILLINOIS

(19) E. Lellmann and M. Buettner, *Ber.*, **23**, 1383 (1890).

(20) J. Abel, *ibid.*, **28**, 3106 (1895); A. M. Clifford, U. S. Patent 1,779,390; *C. A.*, **25**, 233 (1931).

(21) W. W. Groves, British Patent 472,757; *C. A.*, **32**, 1480 (1938).