upon chilling. It was filtered, washed with cold water and dried under vacuum over anhydrous calcium chloride. The yield of crude, red 3-aza-4-amino-5-methyl-*o*-benzoquinone dioxime (III) was 0.30 g. (53.8%) m.p. >215°. After four recrystallizations from water, clusters of tiny red needles, m.p. >250°, were obtained.

In a spot test with sodium pentacyanoaquoferrate the development of a green color indicated the presence of a primary aromatic amine.[11]

Infrared absorption occurred at 1650–1678 cm.$^{-1}$ (6.06–5.96 μ) (azomethine linkage). Absorption was absent in the 6.5 μ region.

Anal. Calcd. for $C_6H_6N_4O_2 \cdot H_2O$: C, 38.71; H, 5.41; N, 30.10; mol. wt., 186. Found: C, 38.81; H, 5.22; N, 30.22; mol. wt., 255.[12]

A sample was dried at 110° and analyzed again.

Anal. Calcd. for $C_6H_8N_4O_2$: C, 42.85; H, 4.80; N, 33.32. Found: C, 42.76; H, 5.00; N, 33.21.

In a similar experiment, ψ-*o*-dinitrosobenzene was reduced by hydroxylamine in diethylamine to the dioxime of *o*-benzquinone in 29.6% yield. The substitution of triethanolamine for diethylamine in both cases brought about a lower yield of product.

Reduction of ψ-1,2-Dinitroso-3,5-dinitrobenzene.—To 50 g. of 48% hydroiodic acid, small portions of ψ-1,2-dinitroso-3,5-dinitrobenzene, m.p. 172°,[13] was added at such a rate that the temperature was held at 50° and until a total of 4.5 g. (0.02 mole) had been added. The mixture was cooled to room temperature and iodine was removed with the addition of sodium sulfite. The dark red precipitate, 1,2-diamino-3,5-dinitrobenzene, separated from methanol as red prisms or needles, m.p. 214–215°,[14] wt. 2.8 g. (60%). The diacetyl derivative was prepared in refluxing acetic anhydride and was recrystallized from alcohol from which it separated as colorless needles, m.p. 244–245°.[15]

Amination of 2-Amino-3-nitropyridine.—To a warm solution of 1.0 g. (7.2 mmoles) of 2-amino-3-nitropyridine in 60 ml. of ethanol was added with swirling 2.50 g. (0.036 mole) of hydroxylamine hydrochloride. While maintaining the mixture at about 50–60° a solution of 5.0 g. (0.09 mole) of potassium hydroxide in 30 ml. of methanol was added over a one hour period. The mixture was warmed for an additional hour and then concentrated on the steam-bath. Addition of small amounts of water resulted in a clear solution which was concentrated until substantially all the alcohol was removed. Separation of 2,6-diamino-3-nitropyridine occurred upon chilling in an ice-bath. It was filtered, washed with water and dried at 80°, wt. 0.10 g. (9.0%), m.p. 235–237° dec. Recrystallization from methanol gave yellowish-green crystals, m.p. 236–236.5° dec. (lit.[16] m.p. 230° dec.).

In a similar manner, 2,6-diamino-3-nitro-5-methylpyridine, m.p. 282° (uncor.) after recrystallization from nitromethane, was obtained in 21% yield from 2-amino-3-nitro-5-methylpyridine.

Anal. Calcd. for $C_6H_8N_4O_2$: C, 42.85; H, 4.80; N, 33.32. Found: C, 42.95; H, 5.05; N, 33.15.

(11) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., New York, N. Y., 3rd ed., 1947, pp. 381–383.

(12) The molecular weight was determined by the ebullioscopic method in acetic acid by the Huffman Micro-analytical Laboratories, Wheatridge, Colorado. These results indicate that an association with one molecule of acetic acid occurred: $C_6H_8N_4O_2 \cdot H_2O \cdot C_2H_4O_2$ has calcd. mol. wt. 246.

(13) P. Drost, *Ann.*, **307**, 49 (1899).

(14) R. Nietzki and H. Hagenback, *Ber.*, **30**, 539 (1897).

(15) L. M. Norton and J. F. Elliot, *ibid.*, **11**, 327 (1878).

(16) A. E. Tschitschibabin and O. A. Zeide, *J. Russ. Phys. Chem. Soc.*, **50**, 522 (1920); *C. A.*, **18**, 1496 (1924).

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM ROHM AND HAAS CO.]

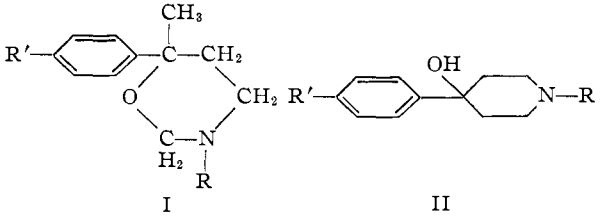
The Aminomethylation of Olefins. IV. The Formation of 1-Alkyl-4-aryl-1,2,3,6-tetrahydropyridines

BY CLAUDE J. SCHMIDLE AND RICHARD C. MANSFIELD

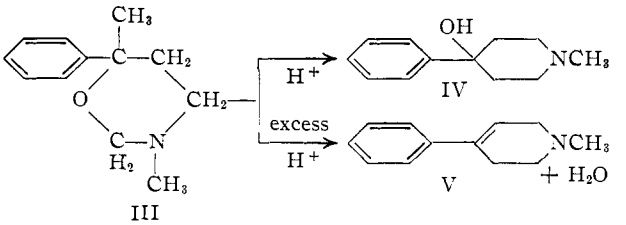
RECEIVED JULY 25, 1955

1-Alkyl-4-aryl-1,2,3,6-tetrahydropyridines and 1-alkyl-4-aryl-4-piperidinols have been obtained by the acid-catalyzed rearrangement of 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines. 1-Alkyl-4-aryl-4-piperidinols have been obtained by hydration of 1-alkyl-4-aryl-1,2,3,6-tetrahydropyridines.

The discovery that 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (I)[1] and 1-alkyl-4-aryl-4-piperidinols (II)[2] are the principal products of the reaction of α-methylstyrenes, formaldehyde and primary amine salts suggested the possibility that 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (I) could be converted to 1-alkyl-4-aryl-4-piperidinols (II). The rearrangement of 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III) was effected using either sulfuric acid or hydrochloric acid. Under relatively mild reaction conditions some 1-methyl-4-phenyl-4-piperidinol (IV) was obtained. The principal product with excess acid was 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V).



I II



III IV V

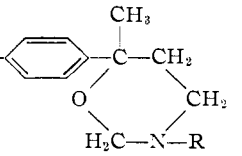
Under conditions similar to those employed for the rearrangement of 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III) to 1-methyl-4-phenyl-1,2,-3,6-tetrahydropyridine (V), 1-methyl-4-phenyl-4-piperidinol (IV) is known[2,3] to undergo dehydration to 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V). When α-methylstyrene, formaldehyde and methylamine hydrochloride reacted and then were treated with excess sulfuric acid, 1-methyl-4-

(1) H. D. Hartough, J. J. Dickert, Jr., and S. L. Meisel, U. S. Patent 2,647,117 (July 28, 1953); *C. A.*, **48**, 8265 (1954).

(2) C. J. Schmidle and R. C. Mansfield, THIS JOURNAL, **77**, 5698 (1955).

TABLE I

3-ALKYL-6-METHYL-6-ARYLTETRAHYDRO-1,3-OXAZINES R′

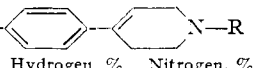


R	R′	Yield,[a] %	B.p. °C.	Mm.	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Methyl	H	42[b]	78–80	0.75	$C_{12}H_{17}NO$	75.35	75.68	8.96	8.97	7.33	7.25
Ethyl	H	36[c]	96–101	1.1	$C_{13}H_{19}NO$	76.05	75.67	9.33	9.40	6.82	7.17
Benzyl	H	57[d]	160–165	0.6	$C_{18}H_{21}NO$	80.86	81.13	7.92	7.86	5.24	5.17
Methyl	CH_3	49[e]	97–102	1.0	$C_{13}H_{19}NO$	76.05	76.50	9.33	9.52	6.82	6.73

[a] Yield based on material boiling within 10° of analytical sample. [b] 30% of corresponding piperidinol also obtained. [c] 12% of corresponding piperidinol also obtained. [d] 7% of corresponding piperidinol also obtained. [e] 30% of corresponding piperidinol also obtained.

TABLE II

1-ALKYL-4-ARYL-1,2,3,6-TETRAHYDROPYRIDINES (BY METHOD A) R′



R	R′	Yield, %	B.p. °C.	Mm.	M.p.,[k] °C.	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found	Chlorine % Calcd.	Found
Methyl	H	86[a]	85–90	0.8	40–42	$C_{12}H_{15}N$	83.19	82.59	8.73	8.71	8.09	8.09		
			Hydrochloride		247–249[l]	$C_{12}H_{16}ClN$	68.72	68.69	7.69	7.81	6.68	6.47	16.9	16.8
Ethyl	H	71[a]	102–107	1.2		$C_{13}H_{17}N$	83.37	82.85	9.15	9.45	7.48	7.61		
			Hydrochloride		192–194	$C_{13}H_{18}ClN$	69.78	69.93	8.11	8.19	6.26	6.25	15 8	15.8
n-Hexyl	H	6[bc]	137–142	0.8		$C_{17}H_{25}N$	83.89	83.26	10.35	10.54	5.76	5.63		
			Hydrochloride		196–198	$C_{17}H_{26}ClN$	72.96	72.68	9.37	9.39	5.01	5.07	12.7	12.6
Allyl	H	23[bd]	110–115	1.2		$C_{14}H_{17}N$	84.37	83.74	8.60	9.09	7.03	7.20		
			Hydrochloride		190–192	$C_{14}H_{18}ClN$	71.32	71.52	7.70	7.82	5.94	5.91	15 0	15.1
Benzyl	H	66[a]	169–174	1.5		$C_{18}H_{19}N$	86.70	86.21	7.68	7.87	5.62	5.57		
Methoxypropyl	H	19[be]	142–143	1.3		$C_{16}H_{21}NO$	77.88	77.91	9.15	9.12	6.06	6.21		
			Hydrochloride		161–163	$C_{16}H_{22}ClNO$	67.27	67.28	8.28	8.33	5.23	5.20	13.2	13.2
Norbornylmethyl	H	44[f]	170–173	1.2		$C_{19}H_{25}N$	85.34	85.19	9.42	9.63	5 24	5.12		
			Hydrochloride		222–224	$C_{19}H_{26}ClN$	75.09	75.28	8.63	8.74	4.61	4.65	11.7	11.7
Dimethylaminoethyl	H	17[b]	130–135	1.2		$C_{15}H_{22}N_2$	78.21	77.61	9.63	10.02	12.16	12.12		
			Hydrochloride		257–259	$C_{15}H_{24}Cl_2N_2$					9.24	9.20	23.4	23.3
Methyl	CH_3	84[a]	105–110	1.2	76–78	$C_{13}H_{17}N$	83.37	83.46	9.15	9.23	7.48	7.44		
			Hydrochloride		202–203	$C_{13}H_{18}ClN$	69.78	70.07	8.11	8.19	6.26	6.25	15.8	15.8
Ethyl	CH_3	17[bg]	116–119	1.3	41–43	$C_{14}H_{19}N$	83.53	82.83	9.51	9.42	6.96	6.90		
			Hydrochloride		183–184	$C_{14}H_{20}ClN$	70.72	70.82	8.48	8.75	5.89	5.86	14.9	15.0
n-Butyl	CH_3	19[bh]	128–133	0.8		$C_{16}H_{23}N$	83.78	83.51	10.11	10.26	6.11	6.20		
Allyl	CH_3	28[bi]	115–125	0.7	40–43	$C_{15}H_{19}N$	84.45	83.90	8.98	9.11	6.57	6.65		
Benzyl	CH_3	42[bj]	168–173	0.7		$C_{19}H_{21}N$	86.64	86.57	8.04	8.14	5.32	5.42		

[a] Yield calculated from oxazine. Redistilled oxazine used as starting material for rearrangement. [b] Yield calculated from starting olefin. Once-distilled crude oxazine used as starting material for rearrangement. [c] 18% of corresponding piperidinol also obtained from olefin; see ref. 2. [d] 27% of corresponding piperidinol also obtained from olefin; see ref. 2. [e] 18% of corresponding piperidinol also obtained from olefin; see ref. 2. [f] Intermediate oxazine not isolated. Yield includes tetrahydropyridine from dehydration of any piperidinol present. [g] 27% of corresponding piperidinol also obtained from olefin; see ref. 2. [h] 27% of corresponding piperidinol also obtained from olefin; see ref. 2. [i] 25% of corresponding piperidinol also obtained from olefin; see ref. 2. [j] 15% of corresponding piperidinol also obtained from olefin; see ref. 2. [k] All m.p.'s uncorrected. Hydrochlorides recrystallized from acetone containing approximately 5% isopropyl alcohol; tetrahydropyridines recrystallized from heptane. [l] Ref. 2 reported 247–249°; A. Ziering, L. Berger, S. D. Heineman and J. Lee, *J. Org. Chem.*, 12, 894 (1947), reported 241–243°; ref. 3 reported 248–250°.

phenyl-1,2,3,6-tetrahydropyridine (V) was obtained directly in 52% yield, being formed both by dehydration of 1-methyl-4-phenyl-4-piperidinol (IV) and by rearrangement of 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III). If the excess acid is added before the reaction of α-methylstyrene, formaldehyde and methylamine hydrochloride is complete and a homogeneous solution has resulted, the yield of basic products is considerably reduced.

Other 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (I) were prepared according to the method of Hartough[1] from α-methylstyrene and *p*-α-dimethylstyrene, formaldehyde and a variety of primary amines. In most cases the once-distilled 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazine (I) was used as the starting material for the rearrangement to 1-alkyl-4-aryl-1,2,3,6-tetrahydropyridine, but several were first purified by redistillation. Those which were purified are shown in Table I.

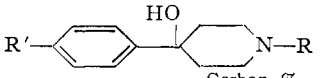
The rearrangement of 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (I) to 1-alkyl-4-aryl-1,2,3,6-tetrahydropyridines using excess hydrochloric acid (method A) was extended and the 1-alkyl-4-aryl-1,2,3,6-tetrahydropyridines prepared are shown in Table II.

Several 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (I) were converted to 1-alkyl-4-aryl-4-piperidinols (II) using milder rearrangement conditions. Because of the similarity in boiling point of corresponding 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (I) and 1-alkyl-4-aryl-1,2,3,6-tetrahydropyridines, no attempt was made to isolate these materials from the lower boiling fractions obtained from this series of reactions. The 1-alkyl-4-aryl-4-piperidinols (II) prepared in this manner are shown in Table III.

1-Alkyl-4-aryl-4-piperidinols (II) also were prepared by hydration of the corresponding 1-alkyl-

TABLE III

1-ALKYL-4-ARYL-4-PIPERIDINOLS[2] BY REARRANGEMENT OF 3-ALKYL-6-METHYL-6-ARYLTETRAHYDRO-1,3-OXAZINES

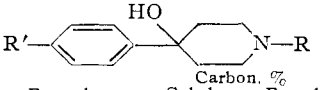


R	R′	Yield, %	M.p., °C. uncor.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl[a]	H	15	115–116[c]	$C_{12}H_{17}NO$	75.35	75.52	8.96	8.83	7.33	7.31
Allyl[b]	H	10	85–87[d]	$C_{14}H_{19}NO$	77.38	77.33	8.81	8.92	6.45	6.41
Benzyl[a]	H	28	106–108[d]	$C_{18}H_{21}NO$	80.86	81.18	7.92	8.07	5.24	5.22

[a] Prepared from redistilled 3-alkyl-6-methyl-6-phenyltetrahydro-1,3-oxazine. [b] Prepared from impure 3-allyl-6-methyl-6-phenyltetrahydro-1,3-oxazine, b.p. 105–120° (0.7 mm.). *Anal.* Calcd: C, 77.38; H, 8.81; N, 6.45. Found: C, 78,75; H, 8.74; N, 6.86. [c] Recrystallized from heptane–toluene mixture. [d] Recrystallized from heptane.

TABLE IV

1-ALKYL-4-ARYL-4-PIPERIDINOLS[2] BY HYDRATION OF 1-ALKYL-4-ARYL-1,2,3,6-TETRAHYDROPYRIDINES

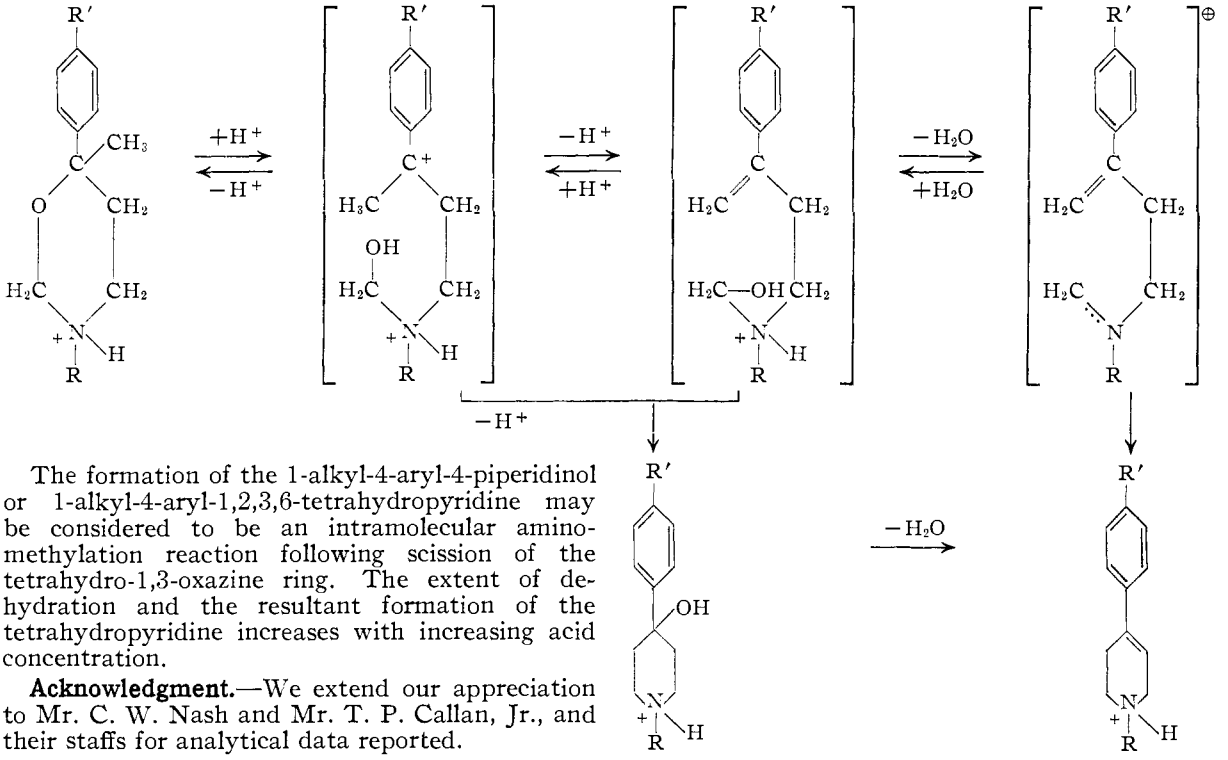


R	R′	Yield, %	M.p., °C. uncor.[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Methyl	H	73	113–115[b]	$C_{12}H_{17}NO$	75.35	75.39	8.96	8.90	7.33	7.22
n-Butyl[c]	H	65	89–90	$C_{15}H_{23}NO$	77.21	77.54	9.93	9.68	6.00	6.08
n-Hexyl	H	74	98–100	$C_{17}H_{27}NO$	78.11	77.81	10.41	10.53	5.36	5.50
n-Butyl	CH_3	56	83–85	$C_{16}H_{25}NO$	77.68	77.84	10.19	10.12	5.66	5.64
Benzyl	CH_3	75	77–79	$C_{19}H_{23}NO$	81.10	80.60	8.24	8.35	4.98	5.03

[a] Recrystallized from heptane unless otherwise stated. [b] Recrystallized from heptane–toluene mixture. [c] Prepared from impure 1-*n*-butyl-4-phenyl-1,2,3,6-tetrahydropyridine, b.p. 124–127° (1.3 mm.). *Anal.* Calcd.: C, 83.66; H, 9.83; N, 6.51. Found: C, 82.85; H, 10.03; N, 6.77.

4-aryl-1,2,3,6-tetrahydropyridines. The method of McElvain and Safranski,[3] involving addition of hydrobromic acid in acetic acid, was used for the preparation of the intermediate 4-bromopiperidines. These were hydrolyzed to give the desired 1-alkyl-4-aryl-4-piperidinols, which are shown in Table IV.

A possible course of the rearrangement reaction may be illustrated as



The formation of the 1-alkyl-4-aryl-4-piperidinol or 1-alkyl-4-aryl-1,2,3,6-tetrahydropyridine may be considered to be an intramolecular aminomethylation reaction following scission of the tetrahydro-1,3-oxazine ring. The extent of dehydration and the resultant formation of the tetrahydropyridine increases with increasing acid concentration.

Acknowledgment.—We extend our appreciation to Mr. C. W. Nash and Mr. T. P. Callan, Jr., and their staffs for analytical data reported.

(3) S. M. McElvain and J. C. Safranski, Jr., THIS JOURNAL, **72**, 3134 (1950).

Experimental

The following typical examples serve to illustrate the general procedure used in each case.

3,6-Dimethyl-6-phenyltetrahydro-1,3-oxazine (III).—This material was prepared by the method of Hartough, *et al.*[1] From a 1.0-mole preparation there was obtained[2] 89 g. of crude 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III) which was redistilled to give 80 g. (42%), b.p. 70–90° (0.75 mm.), of which 38 g. (20%) distilled at 78–80° (0.75 mm.), $n^{25}D$ 1.5278.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.33. Found: C, 75.68; H, 8.97; N, 7.25.

The 1-Methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V). Method A. Hydrochloric Acid.—To 73 g. (0.38 mole) of 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III) was slowly added with external cooling 100 g. (1.0 mole) of concentrated hydrochloric acid. The mixture was stirred on a steam-bath for 6 hr. After cooling it was poured into 300 ml. of water and made basic with excess 50% sodium hydroxide. The amine was taken up in benzene, dried and distilled to give 57 g. (86%) of 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V), b.p. 85–90° (0.8 mm.). This crystallized and melted at 40–42° after recrystallization from heptane.

Method B. Sulfuric Acid.—A similar experiment using 50 g. (0.26 mole) of 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III) and 150 g. (1.0 mole) of 66% sulfuric acid gave 36 g. (80%) of 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V).

Anal. Calcd. for $C_{12}H_{15}N$: N, 8.09. Found: N, 8.04.

The hydrochloride melted at 251–252° after recrystallization from acetone containing a small amount of isopropyl alcohol. A mixed m.p. with the hydrochloride from method A was 249–251°.

Anal. Calcd. for $C_{12}H_{16}NCl$: Cl, 16.9. Found: Cl, 16.9.

A 1.73-g. (0.01 mole) sample took up 0.01 mole of hydrogen over 5% palladium on alumina in 95% ethanol at room temperature and at atmospheric pressure. The picrate of the resulting 1-methyl-4-phenylpiperidine melted at 235–237°, lit.[4] m.p. 236–237°, lit.[5] m.p. 239–240°

Method C. Direct Preparation from α-Methylstyrene, Formaldehyde and Methylamine Hydrochloride.—A mixture of 280 g. (4.15 moles) of methylamine hydrochloride and 680 g. (8.38 moles) of 37% aqueous formaldehyde was stirred and warmed until homogeneous. There was added 472 g. (4.00 moles) of α-methylstyrene and the mixture was stirred vigorously while the temperature was raised to 75°. Heating was discontinued and the ensuing exothermic reaction was controlled by external cooling so that the temperature remained at 90–100°. When the exotherm had subsided the mixture was stirred on a steam-bath for one hour and then cooled to 50°. There was added slowly 340 g. (3.40 moles) of concentrated sulfuric acid with external cooling so that the temperature did not rise above 70°. When the addition was complete the mixture was stirred for 3 hr. at 90–95°, cooled, poured into 2 l. of water and extracted with benzene. The aqueous portion was made basic with excess 50% sodium hydroxide and the amine was taken up in benzene, dried and distilled to give 361 g. (52%) of 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V), b.p. 80–100° (0.9 mm.).

Anal. Calcd. for $C_{12}H_{15}N$: N, 8.09. Found: N, 8.18.

The hydrochloride melted at 250–252° after recrystallization from a 20:1 acetone–isopropyl alcohol mixture. A mixed m.p. with the hydrochloride from method B was 250–252°.

Anal. Calcd. for $C_{12}H_{16}NCl$: C, 68.72; H, 7.69; N, 6.68; Cl, 16.9. Found: C, 68.64; H, 7.72; N, 6.77; Cl, 16.7.

1-Methyl-4-phenyl-4-piperidinol (IV). A. By Rearrangement of 3,6-Dimethyl-6-phenyltetrahydro-1,3-oxazine (III).—A mixture of 96 g. (0.50 mole) of redistilled 3,6-dimethyl-6-phenyltetrahydro-1,3-oxazine (III) and 50 g. (0.51 mole) of 37% hydrochloric acid was stirred on a steam-bath for 5 hours, cooled, poured into 300 ml. of water and made basic with excess 50% sodium hydroxide. The amine was taken up in toluene, dried and distilled to give 72 g. of material, b.p. 84–114° (1.2 mm.), and 14 g. (14.6%) of 1-methyl-4-phenyl-4-piperidinol (IV), b.p. 114–129° (1.2 mm.). This crystallized and after recrystallization from a toluene–heptane mixture melted at 115–116°.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.33. Found: C, 75.52; H, 8.83; N, 7.31.

The lower boiling material contained 7.66% nitrogen.

B. By Hydration of 1-Methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V).—Into a solution of 10 g. (0.058 mole) of 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (V) in 200 ml. of glacial acetic acid was slowly bubbled anhydrous hydrogen bromide during 2 hours while the temperature was maintained at 10–20° by external cooling. The mixture was then allowed to warm to room temperature and stand overnight. The acetic acid was removed by distillation under reduced pressure below 45°. The residue was dissolved in 200 ml. of water at room temperature and then heated on a steam-bath for 2 hours, cooled and made basic with excess 50% sodium hydroxide. The solid amine was filtered off and recrystallized from heptane–toluene to give 8 g. (73%) of 1-methyl-4-phenyl-4-piperidinol (IV), m.p. 113–115°.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.33. Found: C, 75.39; H, 8.90; N, 7.22.

PHILADELPHIA, PENNSYLVANIA

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Reaction of Silver Penta-*O*-acetyl-D-gluconate with Bromine[1]

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When the silver salt of penta-*O*-acetyl-D-gluconic acid is treated with bromine, the carboxylic acid group is lost as carbon dioxide and *aldehydo*-1-bromopenta-*O*-acetyl-D-arabinose is formed. The structure of this compound was proved by converting the compound into known *aldehydo*-D-arabinose hexa-*O*-acetate by means of silver acetate and also by reducing the *aldehydo*-1-bromopenta-*O*-acetyl-D-arabinose to D-arabitol by means of lithium aluminum hydride. D-Arabitol was identified as the penta-*O*-acetate.

One of the authors has reported[2] that the thoroughly dry silver salt of alginic acid (a polymannuronic acid) is decarboxylated when a suspension of the salt in carbon tetrachloride is treated with bromine. The over-all reaction by which this decarboxylation occurs has been extensively investigated[3] on a large number of aliphatic and aromatic acids, and it is known that the aldehyde with one less carbon atom can be obtained from the α-hydroxy acids.[4,5] So far as we are aware, however, the decarboxylation of the sugar acids by the treatment of their silver salts with halogen has not been investigated.

Although the sugar acids can be decarboxylated by treating the corresponding amide with hypochlorite[6] or by treating the calcium salt of the acid with hydrogen peroxide in the presence of

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