Acknowledgments. The author is indebted to Dr. A. R. Hanze for his interest in this work, and to Mr. M. F. Grostic for interpretation of the infrared spectra.

DEPARTMENT OF CHEMISTRY
THE UPJOHN COMPANY
KALAMAZOO, MICH.

Synthesis of Some *N*-Benzyl-*N*-alkyl-*N*-*n*-octylamines

P. J. APICE[1]

Received April 29, 1960

A recent research program of this laboratory involved the preparation of some new tertiary amines from the intermediate *N*-benzyl-*N*-*n*-octylamine. In general, the intermediate *N*-benzyl-*N*-*n*-octylamine can be prepared *via* reduction of the corresponding Schiff base,[2] or by the reaction of benzylamine with an *n*-oxtyl halide, or vice versa. In this work the second method was employed. This method is similar to that used by King and Work[3] in preparing various secondary and tertiary benzylamines.

The scope of the project involved only the *n*-alkyl halides from one to seven carbon atoms. The *N*,*N*-di-*n*-octyl compound was isolated from the intermediate secondary amine when the latter was produced.

The elemental analyses and physical properties are given in Tables I and II. It is worthy to note confirmation of the atomic factor value for the methylene group (D line) for the series synthesized. Calculations from the observed molecular refractivities over the range of one to eight carbon atoms give an M_D value of 4.617, while the generally accepted value is 4.618.[4]

Several attempts to prepare the usual derivatives of the tertiary amines of this series have thus far been unsuccessful. This difficulty is probably due mainly to steric effects.

EXPERIMENTAL[5]

N-Benzyl-N-n-octylamine. This base was obtained as the main product by the following process: Benzylamine, 286 g. (2.67 moles), was mixed with *n*-octyl bromide, 257 g. (1.33 moles), in a large beaker and allowed to stand at room temperature. The reaction is midly exothermic, and after 45 min. benzylamine hydrobromide was deposited as a white slush. The mixture was heated on a boiling water bath for 1 hr., cooled, diluted with dry ether, and the benzylamine

TABLE I

ELEMENTAL ANALYSES

Alkyl	Formula	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
H—	$C_{15}H_{25}N$	68	82.12	83.23	11.49	11.59	6.39	6.13
CH_3—	$C_{16}H_{27}N$	39	82.34	82.99	11.66	11.63	6.00	5.92
C_2H_5—	$C_{17}H_{29}N$	73	82.53	83.01	11.81	11.78	5.66	5.78
n-C_3H_7—	$C_{18}H_{31}N$	61	82.69	83.00	11.95	11.97	5.36	5.19
n-C_4H_9—	$C_{19}H_{33}N$	64	82.84	83.23	12.07	12.18	5.09	5.12
n-C_5H_{11}—	$C_{20}H_{35}N$	59	82.97	83.47	12.19	12.25	4.84	4.80
n-C_6H_{13}—	$C_{21}H_{37}N$	64	83.10	82.81	12.29	12.42	4.61	4.50
n-C_7H_{15}—	$C_{22}H_{39}N$	66	83.20	83.31	12.39	12.45	4.41	4.21
n-C_8H_{17}—	$C_{23}H_{41}N$	—	83.31	83.53	12.46	12.46	4.23	4.11

TABLE II

PHYSICAL PROPERTIES

Alkyl	B.P.,/Mm.	Sp. Gr. $\frac{20}{20}$	n_D^{20}	Molecular Refractivity	
				Calcd.	Obs.
H—	159–161.5/10	0.8914	1.4945	71.54	71.70
CH_3—	150–151.5/9	0.8825	1.4909	76.50	76.57
C_2H_5—	155.5–157/9	0.8796	1.4886	81.12	81.16
n-C_3H_7—	167–169/11	0.8758	1.4857	85.73	85.66
n-C_4H_9—	166–169/8	0.8722	1.4850	90.28	90.43
n-C_5H_{11}—	178.5–180.5/9	0.8702	1.4835	94.97	95.09
n-C_6H_{13}—	185–187.5/8	0.8688	1.4823	99.59	99.65
n-C_7H_{15}—	195–197/8	0.8682	1.4818	104.21	104.23
n-C_8H_{17}—	211–212/9	0.8679	1.4815	108.82	108.89

(1) Present address: Plastics and Coal Chemicals Division, Allied Chemical Corporation, Technical Department, Edgewater, N. J.

(2) R. E. Lutz, *et al.*, *J. Org. Chem.*, **12**, 760 (1947).

(3) H. King and T. S. Work, *J. Chem. Soc.*, 401 (1942).

(4) H. Gilman, *Organic Chemistry, An Advanced Treatise*, Vol. *II*, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1751.

(5) All melting and boiling points are corrected.

hydrobromide collected. Recrystallization of the hydrobromide from ethanol gave a material, m.p. 222–223°.

Anal. Calcd. for $C_7H_{10}NBr$: Br, 42.49. Found: Br, 42.43 and 42.46.

The ethereal solution was shaken with 150 ml. of 10% aqueous sodium hydroxide solution, separated, and dried over potassium hydroxide. The ether was removed by vacuum, and fractionation of the main material through a Vigreux column under reduced pressure gave: Benzylamine, 21 g., b.p. 62–67°/8–9 mm.; *N*-benzyl-*N*-*n*-octylamine, 220 g., b.p. 140–175°/11–12 mm.; and *N*-benzyl-*N*,*N*-di-*n*-octylamine, 45 g., b.p. 191–213°/10 mm. Separate redistillations through the Vigreux column of the latter two cuts gave the desired products. (See Tables I and II for analyses and physical properties.)

General method for preparing the N-benzyl-N-alkyl-N-n-octylamines. *N*-Benzyl-*N*-*n*-octylamine (21.9 g., 0.1 mole), alkyl halide (0.11 mole), and potassium hydroxide (7.7 g.) were added to a suitable flask and refluxed for 5 hr. The product was then cooled, shaken with 50 ml. of 10% aqueous sodium hydroxide solution, and separated. Fractionation of the colorless oily material through a Vigreux column under reduced pressure gave essentially the desired tertiary amine. The main product collected was then redistilled through the Vigreux column to give the *N*-Benzyl-*N*-alkyl-*N*-*n*-octylamine. (See Tables I and II for analytical data and physical properties.)

Acknowledgment. The author wishes to express his thanks to Mr. Anthony Cristino of the Plastics Division, Allied Chemical Corporation, Technical Department, Edgewater, N. J., for the elemental analyses. Gratitude is also expressed to Prof. S. P. Gimelli, Fairleigh Dickinson University, for making the overall research program possible.

CHEMISTRY DEPARTMENT
FAIRLEIGH DICKINSON UNIVERSITY
TEANECK, N. J.

Improved Syntheses of β-Alanine

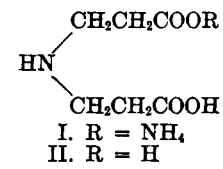
F. POPPELSDORF AND R. C. LEMON

Received May 12, 1960

One important group of β-alanine syntheses includes preparative procedures which involve the interaction at elevated temperatures and pressures of aqueous ammonia and acrylonitrile,[1] esters of acrylic acid,[2] or compounds RCH_2CH_2X which can yield acrylonitrile or acrylic acid by a simple, usually base-catalyzed, elimination reaction[3–6], $RCH_2CH_2X \rightarrow RH + CH_2 = CHX$ (X = CN or COOH). These reactions have generally been carried out between 125 and 250°. In each case, the β-alanine was directly isolated by precipitating it from the concentrated reaction products with a solvent in which it is sparingly soluble, *e.g.*, methanol. Where mentioned, the β-alanine thus obtained is claimed to be of high purity.

Preliminary investigations in this laboratory of syntheses of β-alanine by the interaction of aqueous ammonia and either ethyl or methyl acrylate[2] at 125 to 190°, or ethylene cyanohydrin[4] at 180 to 190°, showed, however, that quite impure β-alanine was invariably produced. In some instances, the product contained less than 70% of β-alanine. The prescribed isolation procedures[2,4] were followed in each case.

The impure products were found by titration to contain acidic and basic functions in almost equivalent amounts; moreover, the neutralization equivalents determined were only slightly greater than those calculated for β-alanine. Combined ammonia[7] (in the form of ammonium salts) was, however, present in appreciable quantities. No unsaturated compounds or tertiary amines were detected. These results, together with an analysis specific for the primary amino group,[8] indicated that the major impurity was probably the monoammonium salt of 3,3′-iminodipropionic acid (I).



I. R = NH_4
II. R = H

Pertinently, Ford[9] has pointed out that the monoammonium salt (I) and acid (II) are probable by-products in β-alanine syntheses of the type under discussion. Compounds I and II have solubilities similar to that of β-alanine in water and methanol,[9] the solvents employed for the isolation. Consequently, if these by-products are formed in large enough quantity they will crystallize with the β-alanine. Furthermore, the similarity of solubilities makes purification by fractional crystallization tedious and impractical.

A simple purification procedure for β-alanine made by syntheses based on an acrylate ester or ethylene cyanohydrin has now been found. Refluxing of either diisopropylamine or triethylamine with an aqueous solution of the crude β-alanine converted the impurities into methanol-soluble products but did not affect the β-alanine. Because β-alanine is sparingly soluble in methanol, the amine treatment followed by precipitation with methanol enabled the direct isolation of the amino-acid in a good degree of purity (95 to 98%). One crystallization of this product from water gave β-alanine in a purity of 99.9%.

(1) G. H. Carlson and C. N. Hotchkiss, U. S. Patent 2,377,401 (1945).
(2) S. H. Babcock, Jr., and B. R. Baker, U. S. Patent 2,376,334 (1945).
(3) P. M. Kirk, U. S. Patent 2,334,163 (1943).
(4) P. M. Kirk and J. H. Paden, U. S. Patent 2,364,538 (1944).
(5) J. H. Paden, U. S. Patent 2,414,389 (1947).
(6) P. M. Kirk, U. S. Patent 2,416,630 (1947).
(7) Determined by the method of K. G. Mizuch and A. Y. Savchenko [*Org. Chem. Ind.* (*U.S.S.R.*), **7**, 24 (1940)].
(8) F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **29**, 1174 (1957).
(9) J. H. Ford, *J. Am. Chem. Soc.*, **67**, 876 (1945).