A Convenient Preparation of *t*-Butylamine

BY JOSEPH V. KARABINOS AND KASPER T. SERIJAN

We wish to report a convenient method for the preparation of relatively large quantities of *t*-butylamine by catalytic hydrogenation of 2,2-dimethylethyleneimine. The imine was prepared according to the method of Cairns,[1] *i. e.*, by the sulfation of 2-amino-2-methyl-1-propanol followed by alkali treatment of the 2-amino-2-methyl-1-propanolsulfuric acid. It is interesting to note that no isobutylamine was detected from the hydrogenation of 2,2-dimethylethyleneimine, a product expected by cleavage of the nitrogen at the tertiary carbon.

Both 2,2-dimethylethyleneimine and *t*-butylamine were obtained in a state of purity and their constants determined and recorded below.

PHYSICAL CONSTANTS OF *t*-BUTYLAMINE AND 2,2-DIMETHYLETHYLENEIMINE

	t-Butylamine	2,2-Dimethylethyleneimine
Boiling point, °C.	45.0	70.5
Refractive index, $n^{20}D$	1.3780	1.4075
Density, d^{t}_{4}	0.7055[a]	0.7902[b]
Freezing point, °C.	−72.65	−47.08

[a] $d^{17.5}_{4}$. [b] d^{24}_{4}.

Experimental

Hydrogenation of 2,2-Dimethylethyleneimine.—A mixture containing 710 g. of 2,2-dimethylethyleneimine and 50 g. of U. O. P. nickel catalyst was hydrogenated in a rocker-type autoclave of 3-liter capacity. At a pressure of 700 lb./sq. inch, and a temperature of 130° the reaction proceeded smoothly and almost the theoretical quantity of hydrogen was consumed. After cooling, the filtered solution was subjected to fractional distillation on a 20 theoretical-plate column. The fraction boiling from 44–46° amounted to 510 g. (70%). The physical constants are recorded above.

***t*-Butylamine hydrochloride** was prepared from the amine and concentrated hydrochloric acid, m. p. 290–291. The recorded[2] value is 291°.

2,2-Dimethylethyleneimine phenylurea was prepared by treating the imine with phenyl isocyanate followed by crystallization from neohexane, m. p. 88–89°.

Anal. Calcd. for $C_{11}H_{14}ON_2$: N, 14.73. Found: N, 14.62.

(1) T. L. Cairns, THIS JOURNAL, **63**, 871 (1941).

(2) F. Klages, G. Nober, F. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

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Studies in the Chromammines. IV. Thermal Decomposition of Luteo Salts[1,2]

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It has been observed by Pfeiffer and others[4] that the luteo salts $[Cr\ en_3]Cl_3 \cdot 3.5H_2O$ and $[Cr\ en_3](NCS)_3 \cdot H_2O$ when heated for several days at 160 and 130°, respectively, yield *cis*-$[Cr\ en_2Cl_2]Cl$ and *trans*-$[Cr\ en_2(NCS)_2]NCS$, respectively, indicating the greater stability of the chloride as compared with the thiocyanate. We have now investigated the relative thermal stabilities of a number of other triethylene- and tripropylenediamine chromic salts.

Preparation of Materials.—The amines were dehydrated according to Putnam and Kobe's directions for dehydrating ethylenediamine.[5] Anhydrous chromic sulfate, triethylenediamine chromic sulfate, and tripropylenediamine chromic sulfate were prepared by the methods of Rollinson and Bailar.[6]

The triethylene- and tripropylenediamine chromic salts were for the most part prepared by metathesis between the chromammine sulfate and the corresponding ammonium salt in 100% excess, both in saturated aqueous solutions. The mixed solution was stirred rapidly while cooled in ice. In the cases of bromide, iodide and thiocyanate, crystallization occurred at once; in the case of the chloride, a few minutes were required. The nitrate and oxalate did not crystallize for several hours. The yellow crystals were filtered and air dried.

The triethylenediamine chromic nitrite, cyanide and cyanate were prepared in similar fashion using potassium salts in place of the corresponding ammonium compounds. These luteo salts are somewhat more soluble than any of the others, and crystallized only after several hours.

Tripropylenediamine chromic chloride was too soluble for preparation by this method. Therefore to a solution of 8.36 g. (0.01 mole) of tripropylenediamine chromic sulfate in 50 ml. of water was added 7.32 g. (0.03 mole) of barium chloride dihydrate dissolved in 50 ml. of water. The mixture was allowed to stand three hours at room temperature and the barium sulfate filtered. The filtrate was allowed to evaporate at room temperature, producing yellow crystals of tripropylenediamine chromic chloride. The salt may also be obtained by the addition of alcohol to the filtrate of the barium sulfate filtration. When produced in this manner it is not visibly crystalline, but is a fine yellow powder.

Thermal Decomposition.—To study the thermal decomposition, the loss in weight of a 1-g. sample of the ammine salt to which a small amount of the corresponding ammonium salt had been added was followed over a period of hours as described previously.[1] The temperatures at which significant decomposition occurred with the different salts are shown in Table I.

The triethylenediamine salts, except the previously studied thiocyanate and chloride, decomposed to a brown solid whose composition varied apparently with the temperature and the

(1) For the preceding paper in this series see Rollinson and Bailar, THIS JOURNAL, **66**, 641 (1944).

(2) Presented at the 108th Meeting of the American Chemical Society, New York, N. Y., September 12, 1944.

(3) Abstracted from a portion of a thesis submitted in partial fulfilment of the requirement for the degree of Doctor of Philosophy in Chemistry at the University of Illinois, 1940.

(4) Pfeiffer, Koch, Lando and Trieschmann, *Ber.*, **37**, 4269, 4277 (1904).

(5) Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, 610 (1938).

(6) Rollinson and Bailar, THIS JOURNAL, **65**, 250 (1943).

TABLE I

DECOMPOSITION TEMPERATURES (RELATIVE THERMAL STABILITY) OF CHROMIUM TRIALKYLENEDIAMINE SALTS

Salt	Triethylene, temp., °C.	Tripropylene, temp., °C.
Thiocyanate	130	110
Nitrite	135	...
Nitrate	140	...
Cyanate	150	...
Chloride	160	175
Iodide	200	...
Sulfate	210	...
Bromide	210	195
Cyanide	230	...
Oxalate	280	...

time of heating so that no definite product could be identified. The nitrite and nitrate at slightly higher temperatures, namely, 135 and 140°, respectively, decomposed completely into chromium oxide.

Tripropylenediamine bromide and iodide also decomposed into a dark brown substance indistinguishable from the corresponding product formed by the triethylenediamine salts. The chloride, however, was converted completely after five hours at 175° to the purple *cis*-dichloropropylenediamine chromic chloride. Prolonged heating or the use of higher temperatures should be avoided because these conditions cause a pronounced darkening of the purple salt. After darkening, the salt turns black and then chars. Recrystallization of the purple salt is difficult because of its high solubility.

Anal. Calcd. for $[Cr\ pn_2Cl_2]Cl$: Cr, 16.94. Found: Cr, 16.75.

Similarly the thiocyanate gave a red-orange product at 110°. The product was difficultly soluble in cold water and quite soluble in hot, so was easily crystallized.

Anal. Calcd. for $[Cr\ pn_2(NCS)_2](NCS)$: Cr, 12.88. Found: Cr, 12.98.

The stabilities of the tripropylenediamine salts are in the same order as, and in general appear to be slightly less than, the corresponding triethylenediamine salts.

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The Biosynthesis of Pantothenic Acid[1]

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The biosynthesis of pantothenic acid has been thought to involve a coupling of β-alanine with α-hydroxy-β,β-dimethyl-γ-butyrolactone (pantoyl lactone).[2,3] Organisms requiring pantothenic acid for growth may not be able to synthesize it for one of several reasons. Some, such as lactic acid bacteria, are unable to carry out the coupling. They fail to grow on a mixture of β-alanine and pantoyl lactone, but require the intact pantothenic acid molecule.[4] In the pantothenicless mutant of *Neurospora* (5531), which has this same requirement, the coupling is under genetic control.[5] Other organisms like certain yeasts[6] and a diphtheria bacillus,[2] will grow if pantothenic acid or β-alanine is supplied but cannot use the pantoyl moiety alone. Apparently the pantoyl moiety is manufactured in these organisms and coupled with the added β-alanine to form pantothenic acid. Only the synthesis of β-alanine has been impaired. In still other organisms like *Acetobacter*,[7] a strain of *Proteus morganii*[8] and a hemolytic streptococcus,[2] the synthesis of β-alanine presumably is carried out, but the pantoyl moiety is not made. Again the capacity for coupling has not been lost since pantoyl lactone is able, even if incompletely, to replace pantothenic acid as a growth factor in the medium.

In the course of studies on the nutrition of *Clostridium septicum* we have observed that pantoyl lactone will completely replace pantothenic acid. For these experiments a single cell isolate (strain 59 Li A) was used. The clostridia were grown on a chemically defined medium which is a modification of that proposed by Bernheimer.[9] Growth was measured turbidometrically, the extinction being proportional to the milligrams of bacterial nitrogen as determined by a micro Kjeldahl on washed cultures. At 37° growth was complete in about twelve hours.

The presence of adequate amounts of calcium *d*-pantothenate, sodium *dl*-pantoate or *dl*-pantoyl lactone in the medium resulted in a maximum yield of 16–17 mg. of bacterial nitrogen per 100 cc. (Table I). Each of these substances also supported the maximum rate of growth on this medium. During the logarithmic growth phase one cell generation was produced every sixty to sixty-five minutes. However, on a molar basis calcium *d*-pantothenate is the more active. The molar concentration required to yield 8 mg. of bacterial nitrogen per 100 cc. was 0.2×10^{-6}, while *ca.* 4×10^{-6} *M* *d*-pantoyl lactone or sodium *d*-pantoate was required for the same crop (Fig. 1). When the pantoate concentration is calculated in terms of undissociated *d*-pantoic acid (pK_a = 4.0), its activity per mole is still less than that of undissociated *d*-pantothenic acid (pK_a = 4.4) but

(1) This work was supported in part by a grant from the Josiah Macy, Jr., Foundation.

(2) R. J. Williams, "Advances in Enzymol.," **3**, 253 (1943).

(3) H. R. Rosenberg, "Chemistry and Physiology of the Vitamins," Interscience Publishers, Inc., New York, N. Y., 1942, p. 263.

(4) V. H. Cheldelin, E. H. Hoag and H. P. Sarett, *J. Bact.*, **49**, 41 (1945).

(5) E. L. Tatum and G. W. Beadle, *Growth*, **6**, 27 (1942).

(6) v. N. Nielson and V. Hartelius, *Naturwissenschaften*, **45/46**, 550 (1943); H. P. Sarett and V. H. Cheldelin, *J. Bact.*, **49**, 31 (1945).

(7) L. A. Underkofler and A. C. Banty, *ibid.*, **45**, 183 (1943).

(8) G. Ivanovics, *Z. physiol. Chem.*, **276**, 33 (1942).

(9) A. W. Bernheimer, *J. Exp. Med.*, **80**, 321 (1944). Our medium differs essentially from that of Bernheimer in that the casamino acids were Norite treated, 0.2% of neutralized cysteine hydrochloride replaced the thioglycolic acid and the final medium was sterilized by autoclaving.