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.

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[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$_3$·3.5H$_2$O and [Cr en$_3$](NCS)$_3$·H$_2$O when heated for several days at 160 and 130°, respectively, yield *cis*-[Cr en$_2$Cl$_2$]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

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[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).