[Contribution from the Chemical Laboratory of Stanford University]

THE PREPARATION OF SYMMETRICAL METHYL ISOPROPYL HYDRAZINE AND METHYL ISOPROPYL DI-IMIDE

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Received November 5, 1928 Published March 6, 1929

The author has recently studied the rate of thermal decomposition of the gases of azomethane[2] (dimethyl di-imide) and azo-*iso*propane[3] (di-*iso*propyl di-imide). Their decomposition was found to be homogeneous and unimolecular. A study of the mixed azo compound methyl *iso*propyl di-imide would be valuable in indicating the mechanism of the decomposition and would provide a further test of various theories of unimolecular reactions. This compound had, however, never been prepared, nor had the corresponding hydrazine from which the azo compound could be prepared by oxidation. The preparation of these two new compounds is the first synthesis reported in the literature of a simple mixed aliphatic symmetrical hydrazine or of a mixed aliphatic azo compound.

A method of preparing the hydrazine derivative was suggested by Lochte, Bailey and Noyes.[4] By this method the hydrazone formed by treating methyl hydrazine with acetone would be reduced with hydrogen and colloidal platinum. This procedure was tried. An impure sample of the hydrazone was obtained but it could not be successfully reduced. In this connection it is significant that the reduction of the azine formed from hydrazine and acetaldehyde with hydrogen and platinum catalyst yields a gummy sirup from which no hydrazine derivative could be recovered. This method works well in the preparation of those symmetrical hydrazine derivatives having *iso*propyl or heavier radicals. It seems likely, therefore, that catalytic reduction will not succeed as a general method for the preparation of the simpler aliphatic hydrazines.

Preparation of Symmetrical Methyl *Iso*propyl Hydrazine.—The successful method is indicated by the following equations

$$\mathrm{C_3H_7(COC_6H_5)N-NH(COC_6H_5) + (CH_3)_2SO_4 + NaOH = C_3H_7(COC_6H_5)N-N(COC_6H_5)CH_3 + NaHSO_4 + CH_3OH} \quad (1)$$

$$\mathrm{C_3H_7(COC_6H_5)N-N(COC_6H_5)CH_3 + 2H_2O = C_3H_7NH-NHCH_3 + 2C_6H_5COOH} \quad (2)$$

Dibenzoyl *iso*propyl hydrazine was prepared by the procedure of Lochte, Bailey and Noyes.[4] This was methylated with methyl sulfate to give dibenzoyl methyl *iso*propyl hydrazine.

The dibenzoyl *iso*propyl hydrazine was dissolved in the smallest possible amount of 95% alcohol. To this was added with constant stirring equal molal amounts of

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[2] Ramsperger, This Journal, **49**, 912, 1495 (1927).

[3] Ramsperger, *ibid.*, **50**, 714 (1928).

[4] Lochte, Bailey and Noyes, *ibid.*, **43**, 2597 (1921); **44**, 2556 (1922).

methyl sulfate and concentrated sodium hydroxide solution. One-fourth of the total amounts of each were separately added and when in about one hour the alkaline solution became acid, another fourth was added and so on, and finally an excess of 10 to 20% was added. A greater excess decreased the yield. The product was precipitated from solution by adding four volumes of water with constant stirring. The yield of crude product was 80% of that calculated. It melts at 63–68°, It was purified by dissolving in alcohol and adding water, by crystallizing from ether or by dissolving in ether and adding petroleum ether. The yield was reduced to about 70% and the melting point was then 74–76°. Several recrystallizations gave a melting point of 76.25 to 76.75°.

The once purified product was hydrolyzed by adding five times its weight of concentrated hydrochloric acid and heating on a steam-bath. Benzoic acid soon separated quantitatively. The benzoic acid was filtered off and the remaining solution was concentrated to a very small volume under reduced pressure. It was not possible to isolate the hydrochloride salt by taking up the sirupy residue with absolute alcohol. It was found later that this was due to the extremely hygroscopic nature of this salt. When pure symmetrical methyl *iso*propyl hydrazine was dissolved in dry ether and dry ether containing an equivalent amount of hydrogen chloride was added, a salt formed at once but became pasty due to the absorption of water while being rapidly filtered.

The sirupy residue was treated with concentrated sodium hydroxide solution (1 to 1) in the presence of pure nitrogen gas at reduced pressure (5 to 40 cm.). The methyl *iso*propyl hydrazine forms an upper layer which is distilled into a vessel containing sodium hydroxide sticks. The first container was then sealed off. After about twenty-four hours the upper liquid layer was distilled into a container with aluminum amalgam, after another twenty-four hours into another container with aluminum amalgam and finally fractionally distilled. The temperature and pressure of each distillation were carefully noted. The yield of pure product was 50%.

The fractional distillation showed that most of the material distilled between 79.5 and 79.7° at a pressure of 37.1 cm., but the first fourth of it distilled from about 78.0 to 79.5°. The lower-boiling fraction probably contained some of the lower-boiling azo compound. Samples of the high-boiling fraction were distilled in vacuum into small bulbs which were used for density determinations and for titrations. Titrations with hydrochloric acid and with iodine by the method of Stollé[5] both indicated a purity of 99.7 to 99.8%. The density was 0.7959 ± 0.0005. This value lies between that for symmetrical dimethyl hydrazine (0.8274) and that for symmetrical di-*iso*propyl hydrazine (0.7844). The boiling point under 76 cm. pressure was obtained from the various distillation temperatures and pressures. In Fig. 1 is plotted the logarithm of the distillation pressure in cm. as ordinate and the reciprocal of the absolute temperature of boiling as abscissa. The curve on the left is for methyl *iso*propyl hydrazine and that on the right for methyl *iso*propyl di-imide. The circles were taken from the data of the last two distillations and the cross is the value obtained from the fractional distillation. Since all of these points fall on the same curve, there was no change in the boiling point during the final treatment with aluminum amalgam. The points fall very nearly on a straight line as required by the Clapeyron equation (if ΔH is assumed

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[5] Stollé, *J. prakt. Chem.*, [2] **66**, 332 (1902). See also ref. 4.

constant) and by extrapolation the boiling point at 76 cm. pressure is found to be 100.2 ± 0.5°. This boiling point falls between that of symmetrical dimethyl hydrazine (81°) and that of symmetrical di-*iso*propyl hydrazine (124.5°). The heat of vaporization as given by the slope of the curve of Fig. 1 is found to be 9150 cal. per mole.

This method of preparation should be applicable for other mixed symmetrical hydrazines.

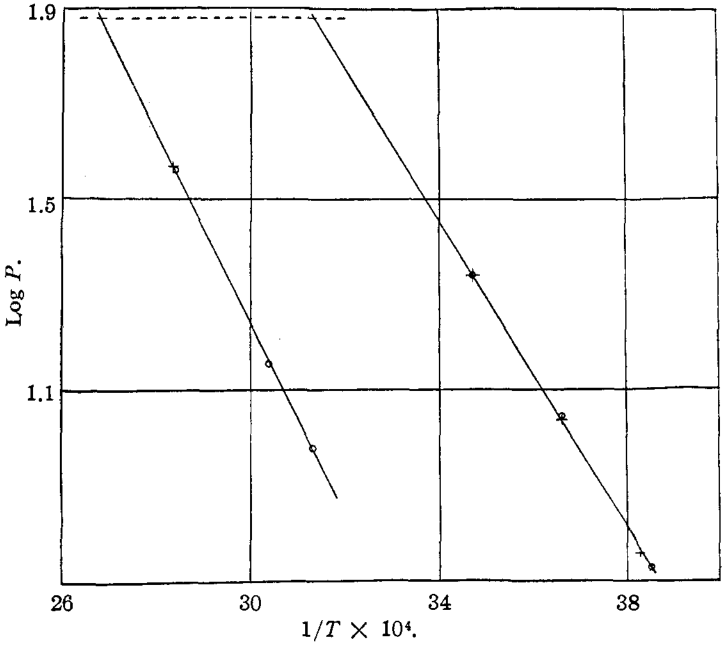

Fig. 1.

Preparation of Methyl *Iso*propyl Di-imide.—Oxidation of the symmetrical methyl *iso*propyl hydrazine by cupric oxide in the presence of a small excess of concd. hydrochloric acid gave a rather poor yield of the azo compound which was probably contaminated by the higher-boiling isomeric hydrazone. Oxidation of the pure symmetrical methyl *iso*propyl hydrazine with 30% hydrogen peroxide was more successful. The oxidation was carried out on a vacuum line with about 20 cm. of nitrogen at the start. A 50% excess of hydrogen peroxide was added to the symmetrical methyl *iso*propyl hydrazine. The reaction mixture was surrounded by an ice-bath and allowed to remain for half an hour. Then the pressure was gradually reduced and the methyl *iso*propyl di-imide distilled out of the solution. The gas passed through a tube containing solid sodium bisulfate and calcium chloride, then through a stopcock and was condensed in a tube immersed in an ether–carbon dioxide snow mixture. The stopcock was closed and the liquid evaporated back and forth between two receivers with a calcium chloride tube between them. Non-condensable gases were pumped off several times. Finally the liquid was distilled through a long, upright tube which was cooled with carbon dioxide snow. The gas was allowed to escape very slowly through a stopcock and was condensed in ether–carbon dioxide mixture. The yield was only about

25%. This was due to the rather small quantities prepared and much was lost in the purification process just described.

The purity and boiling point of the liquid were determined from vapor-pressure data. Vapor pressures were determined at three temperatures before distilling one of the samples and then again after distilling about half of the sample. Two-thirds of the sample was collected for experiments on its thermal decomposition. The vapor-pressure data on this sample are plotted on the right part of Fig. 1. The circles represent the first vapor pressures and the crosses the later ones. It is apparent that there was practically no change in the vapor pressures during distillation, which indicates a pure sample. The boiling point was found by extrapolation to be 46.0 ± 0.5°. The heat of vaporization is 7350 cal. per mole.

Due to the explosive nature of aliphatic azo compounds no analysis was made. The identity of the compound was proved by its properties. It has a slight yellow color and its odor is similar to that of dimethyl di-imide. Its boiling point is between that for dimethyl di-imide (1.5°) and that for di-*iso*propyl di-imide (88.5°). The isomeric hydrazone has a higher boiling point (about 90°). The distinguishing properties of azo compounds given by Lochte, Bailey and Noyes[4] are evidently found in this compound. In addition, its thermal decomposition is a very specific test for an azo compound. Preliminary measurements on its decomposition show that methyl *iso*propyl di-imide decomposes in a homogeneous, unimolecular manner, giving about two moles for each mole of azo compound. It decomposes at about the same rate at 300° as dimethyl di-imide does at 320° and di-*iso*propyl di-imide at 280°. It deviates from the unimolecular rate constant only at pressures below several millimeters. Dimethyl di-imide deviates at pressures below several cm. while di-*iso*propyl di-imide does not show a reduction in rate even at 0.25 mm. This new mixed azo compound is therefore intermediate in its thermal decomposition.

The completed experiments on the thermal decomposition will be published later.

Summary

Symmetrical methyl *iso*propyl hydrazine has been prepared by methylating dibenzoyl *iso*propyl hydrazine with methyl sulfate and hydrolyzing the product in hydrochloric acid solution. The hydrazine derivative is obtained from the acid solution by adding concentrated sodium hydroxide in an atmosphere of nitrogen. It was dried with aluminum amalgam. Methyl *iso*propyl di-imide was prepared by the oxidation of this hydrazine derivative with hydrogen peroxide. It is a typical azo compound in physical properties and in its thermal decomposition.

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