[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Trimethylhydrazine and Tetramethylhydrazine[1]

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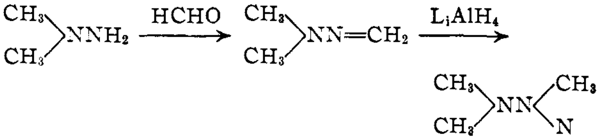
RECEIVED FEBRUARY 19, 1953

Trimethylhydrazine and tetramethylhydrazine have been synthesized Their boiling points, melting points, refractive indices, densities and basic dissociation constants have been measured. A comparison of the boiling points of the methylhydrazines, methylamines and hydrocarbons of similar structure has been made. There is a similar trend for the two series, relative to the hydrocarbons, attributable to the decrease of hydrogen bonding on introducing methyl groups into hydrazine and ammonia, respectively. The decomposition of N-trimethylamine-N′-methylimide is discussed.

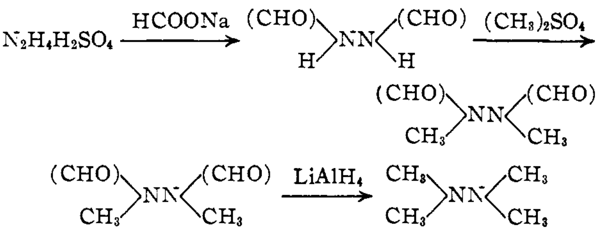
The methyl-substituted hydrazines are being studied in this Laboratory. To complete the series, two new compounds, trimethylhydrazine and tetramethylhydrazine, unknown in spite of previous efforts to prepare them, had to be synthesized. Klages and co-workers, who reported the synthesis of the first tri- and tetraalkylhydrazines, sought to prepare these compounds by various routes.[3] The attempted coupling of two dimethylchloramine molecules using copper–bronze and the reaction between dimethylchloramine and dimethylamidomagnesium halide both resulted in disproportionation of the molecules to amines. The reaction between aqueous formaldehyde and hydrazine hydrochloride yielded only polymerization products. Only hydrazonium salts resulted from methylation attempts with methyl *p*-toluenesulfonate, trimethyl phosphate and trimethyl phosphite. Although successful with higher homologs, the alkylation of hydrazine at elevated temperatures failed with methyl chloride. Klages did succeed in condensing formaldehyde and N,N-dimethylhydrazine to methylenedimethylhydrazine. Attempted catalytic reduction of this compound failed due to resinification on the catalyst.

The methods used in this investigation, with success, followed the equation given below.

Trimethylhydrazine[4]



Tetramethylhydrazine



The reductions with lithium aluminum hydride proceeded smoothly. Even though an excess of reducing agent was used, no cleavage of the N–N bond to produce amine was observed. If the reductions are successful with other hydrazones and hydrazides, the methods may become useful preparations for the other alkylhydrazines.

The compounds prepared are clear, colorless, volatile liquids possessing an offensive odor. They are hygroscopic, reduce hot Fehling solution only slightly, and are stable relative to the other methylhydrazines.

The physical properties of trimethylhydrazine and tetramethylhydrazine are listed in Table I. Methylenedimethylhydrazine has been included because of its similarity to the other methylhydrazines.

TABLE I

PHYSICAL PROPERTIES

	Trimethyl-hydrazine	Tetra-methyl-hydrazine	Methylene-dimethyl-hydrazine
B.p., °C. (mm.)	60 (735)	73 (730)	72 (730)
M.p., °C.	-73^a	-118 ± 10	-103 ± 10
n^{20}_D	1.4039	1.4040	1.4338
d^{20}	0.7716	0.7794	0.8125
K_b	6×10^{-8}	2×10^{-8}	......
E^b	7.1 ± 0.5 (29°)	......	9.1 ± 0.5 (28°)

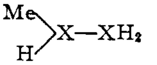
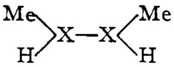
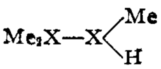
[a] This value is from the heat capacity measurements of J. L. Wood, which will be published shortly. [b] Dielectric constant.

Assuming that the difference between the boiling point of an organic nitrogen compound and the structurally analogous hydrocarbon is caused by hydrogen bonding, a simple subtraction should give a measure of this effect. This is done for hydrazine and the methylhydrazines in Table II and for ammonia and the methylamines in Table III. The similarities of the ΔT values in the tables are immediately seen. This shows that the effect of hydrogen bonding in the two series is about the same.

TABLE II

BOILING POINT COMPARISON OF HYDRAZINES WITH ANALOGOUS SATURATED HYDROCARBONS

(Me = methyl)

Structure	X = CH	Ref.	X = N	Ref.	ΔT
H_2X–XH_2	−89	5a	113	7	201
	−42	5b	87	7	129
	−1	5c	81	8	82
Me_2X–XH_2	−12	5d	63	8	75
	28	6	60		32
Me_2X–XMe_2	**58**	**6**	**73**		**15**

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[1] This research is part of a program of the Chemistry Branch of the Office of Naval Research (Contract N6-ONR-269, Task Order III).

[2] Allied Chemical and Dye Corporation Fellow, 1951–1952.

[3] F. Klages, G. Nober, K. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

[4] J. B. Class and J. G. Aston, THIS JOURNAL, **73**, 2359 (1951), have given a preliminary report of the synthesis of trimethylhydrazine.

TABLE III

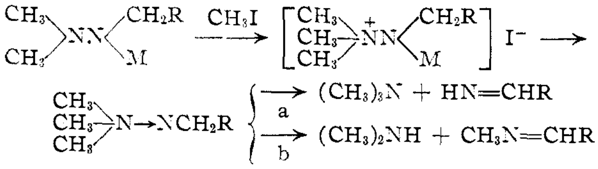
BOILING POINT COMPARISON OF AMINES WITH ANALOGOUS SATURATED HYDROCARBONS

(Me = methyl)

Structure	X = CH	Ref.	X = N	Ref.	ΔT
XH_3	−162	6	−33	7	129
$MeXH_2$	− 88	6	− 6	7	82
Me_2XH	− 42	6	7	7	49
Me_3X	− 12	6	3	7	15

The reaction between methyl iodide and the lithium–aluminum complex of trimethylhydrazine was investigated as a method of preparation of tetramethylhydrazine. Contrary to expectations, the nitrogen–nitrogen bond was cleaved producing the methylamines and ammonia in the following yields: ammonia, 16%; methylamine (assumed), 1%; dimethylamine, 14%; and trimethylamine, 22%. All except methylamine were identified in the mixture by preparation of derivatives. The yields were determined by titration of the chloroform soluble and insoluble hydrochlorides, and are only approximate.

Klages reported similar results for the reaction of methyl bromide with N,N-dimethyl-N′-ethylhydrazidomagnesium chloride.[3] The results of both reactions can be explained if an intermediate analogous to an amine oxide is assumed.



R is H or CH_3. M is an equivalent of metal ion

The Schiff base structures can be either hydrolyzed or polymerized. The decompositions by paths (a) and (b) are analogous to those of trialkylamine oxides.[9] Path (a) corresponds to yielding atomic oxygen, the nitrogen-free radical having undergone an obvious rearrangement. Path (b) corresponds to the decomposition yielding a secondary amine and an aldehyde.

Experimental

N,N-Dimethylhydrazine.—The N,N-dimethylhydrazine was prepared by the reduction of nitrosodimethylamine with zinc dust and acetic acid, as described by Hatt.[10] The product was collected as an aqueous solution of about 75% concentration.

Methylenedimethylhydrazine.—In a 500-ml. round-bottom flask equipped with an addition funnel and stirrer was placed 132 ml. (1.4 moles) of N,N-dimethylhydrazine solution. While stirring, 128 g. (1.6 moles) of 37% formaldehyde solution was added keeping the temperature at 25–30°. The reaction mixture was then saturated with sodium hydroxide, the solution still being stirred. The upper layer of product was separated, and dried and distilled from sodium hydroxide three times. It was finally dried and fractionated from calcium hydride. Product was collected from 70–72°; yield 78–83 g. (78–83%). *Anal.* Calcd.: C, 49.96; H, 11.18; *MR*, 22.97. Found: C, 50.28, H, 10.98; *MR*, 23.14.

Trimethylhydrazine.—A 1-l. round-bottom three-necked flask was equipped with a stirrer, addition funnel and reflux condenser. To 300 ml. of an ether solution of lithium aluminum hydride (12.6 g., 0.33 mole $LiAlH_4$) in the flask, 98.5 ml. (80 g., 1.11 moles) of methylenedimethylhydrazine was added at a rate just fast enough to reflux the ether (addition took 3 hr.). The reaction mixture was stirred and refluxed for 1 hr. longer. Water was then added carefully and the mixture was poured into about 200 g. of ice. After addition of 500 ml. of 6 *N* hydrochloric acid, the resulting solution was concentrated on a steam-bath to about 200 ml.

A 1-l. round-bottom, two-necked flask was fitted with an addition funnel and a condenser set for distillation. The hydrochloride solution was carefully added to a hot solution of 280 g. of sodium hydroxide in 120 ml. of water in the flask. The distillate, which was collected until the temperature reached 100°, was saturated with sodium hydroxide, the temperature being kept below 30° by cooling and stirring. The product was separated, dried and distilled from sodium hydroxide twice. The final drying was over calcium hydride, from which it was fractionated. Product was collected from 58.8–60.1°; yield 57–61 g. (69–74%). *Anal.* Calcd.: C, 48.61; H, 13.60; N, 37.79; mol. wt., 74.13; *MR*, 23.14. Found: C, 48.75; H, 13.33; N, 37.35; mol. wt., 74.2 (potentiometric titration), 68.4 (cryoscopic in water), 75.0 (vapor density); *MR*, 23.49.

N,N′-Diformylhydrazine.—The procedure used was described by Pellizzari.[11] A continuous extraction of the product was introduced in place of the hand extraction.

N,N′-Diformyl-N,N′-dimethylhydrazine.—The method used was essentially that described by Thiele.[12] In an attempt to improve the yield, an excess of dimethyl sulfate was used; and ether was replaced by chloroform in the extraction. Results were erratic and yields varied from 30–78% of the theoretical.

Tetramethylhydrazine.—A 1-l. round-bottom, three-necked flask was fitted with a stirrer, addition funnel and reflux condenser. In the flask was placed 23.0 g. (0.60 mole) of lithium aluminum hydride. About 500 ml. of ether dried over calcium hydride was distilled in, and stirring was started to hasten solution.

After addition was effected, 58 g. (0.50 mole) of N,N′-diformyl-N,N′-dimethylhydrazine was added at a rate rapid enough to reflux the ether. The hydrazine in the addition funnel was kept fluid by using an infrared lamp. Stirring and refluxing was continued for 1 hr. after addition was completed. After 150 ml. of water was added carefully, the ether was stripped off through a fractionating column. Then 80 g. of sodium hydroxide in 100 ml. of water was added and the mixture distilled until the temperature reached 100°. The distillate was saturated with sodium hydroxide while being stirred with the temperature kept below 30°. The product was separated, dried and distilled from sodium hydroxide. The final drying was over calcium hydride, from which it was fractionated. Product was collected from 72.0–73.1°. A yield of approximately 15% was obtained as an average of several preparations, none of which were free from mechanical difficulties preventing complete isolation. *Anal.* Calcd.: C, 54.50; H, 13.72; N, 31.78; mol. wt., 88.15; *MR*, 27.81. Found: C, 54.20; H, 13.61; N, 31.14; mol. wt., 90.4 (potentiometric titration), 84.0 (cryoscopic in water), 87.6 (vapor density); *MR*, 27.66.

Reaction of Methyl Iodide with the Lithium–Aluminum Complex of Trimethylhydrazine.—In the same manner as described in the preparation of trimethylhydrazine, 44.5 ml. (36 g., 0.5 mole) of methylenedimethylhydrazine was added to 143 ml. (6.0 g., 0.16 mole) of an ether solution of lithium aluminum hydride. Addition of 34 ml. (77.5 g., 0.55 mole) of methyl iodide followed at a rate which just refluxed the ether. After 2.5 hr. stirring and refluxing,

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(5) (a) R. K. Witt and J. D. Kemp, THIS JOURNAL, **59**, 273 (1937); (b) J. D. Kemp and C. J. Egan, *ibid.*, **60**, 1521 (1938); (c) J. G. Aston and G. H. Messerly, *ibid.*, **62**, 1917 (1940); (d) J. G. Aston, R. M. Kennedy and S. C. Schumann, *ibid.*, **62**, 2059 (1940).

(6) G. Egloff, "Physical Constants of Hydrocarbons, I," Reinhold Publ. Corp., New York, N. Y., 1939.

(7) "International Critical Tables, I," McGraw-Hill Book Co., New York, N. Y., 1926.

(8) I. Heilbron, "Dictionary of Organic Compounds, I," Oxford University Press, New York, N. Y., 1946, p. 926.

(9) T. Taylor and W. Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford, 1945, p. 167.

(10) H. H. Hatt, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 211.

(11) G. Pellizzari, *Gazz. chim. ital.*, **39**, 529 (1909).

(12) J. Thiele, *Ber.*, **42**, 2576 (1909).

water was carefully added. The mixture was poured onto about 150 g. of ice and then 250 ml. of an hydrochloric acid solution was added. The solution was concentrated by evaporation on a steam-bath.

A 1-l. round-bottom, two-necked flask was fitted with an addition funnel and a condenser set for distillation. A trap containing hydrochloric acid was connected to the receiver. The solution of hydrochlorides was added to a hot solution of 140 g. of sodium hydroxide in 60 ml. of water in this flask. Liquid was distilled until the temperature reached 100°. The distillate was saturated with sodium hydroxide and the evolving gases passed through the hydrochloric acid trap. No hydrazine layer separated. The solution was further degassed by 0.25 hr. boiling after completion of the saturation. The dried hydrochlorides from the trap weighed 41 g.

Ammonia was identified as ammonium chloride, dimethylamine as the benzenesulfonamide and trimethylamine as the picrate. Solubility separations with *n*-butyl alcohol–chloroform indicated that the presence of methylamine could be in no more than trace quantities.

The quantitative distribution of the amines reported above was calculated from the titration of the chloroform soluble and insoluble hydrochlorides with standard silver nitrate.

The values of the basic dissociation constants reported in Table I were obtained from the hydrogen ion concentrations measured during the potentiometric titrations to determine the equivalent weights. The dielectric constants were obtained by a beat frequency method in an apparatus loaned by Prof. W. C. Fernelius.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, FOUAD I UNIVERSITY]

Experiments with Derivatives of Quinone Imides

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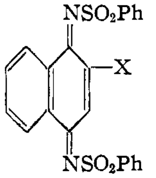
RECEIVED JANUARY 12, 1953

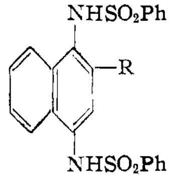
1,4-Naphthoquinone dibenzenesulfonimide (Ia) reacts with Grignard reagents to give the corresponding 2-substituted naphthalene-1,4-dibenzenesulfonamides IIa–IIe together with naphthalene-1,4-dibenzenesulfonamide (II, R = H). Ib, IIIa, IIIb and IV are readily reduced by Grignard reagents to the corresponding di-amides. The mixture (Mg + MgI_2) and lithium aluminum hydride effect the reduction of quinone imides (Ia, Ib, IIIa, IIIb and IV) to the corresponding di-amides. The action of diphenyldiazomethane on Ia and IIIa and the action of 9-diazofluorene on Ia led to the formation of the corresponding cyclopropane derivatives VIII, IX and X, respectively, probably *via* the formation of XI in the case of VIII.

Grignard reagents react with substituted and unsubstituted quinones to give mixtures resulting from 1,4-addition, from addition to carbonyl group, and from reduction.[1]

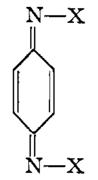
Quinone imides resemble quinones in many of their reactions.[2] We have investigated the action of Grignard reagents on quinone imides.[3] When the yellow 1,4-naphthoquinonedibenzenesulfonimide (Ia) is treated with methyl-, ethyl-, *n*-propyl-, *n*-butyl- and phenylmagnesium halides, the corresponding 2-substituted naphthalene-1,4-dibenzenesulfonamides (IIa–IIe, respectively) are obtained together with the reduction product of Ia, namely, naphthalene-1,4-dibenzenesulfonamide (II, R = H). The addition of the Grignard reagents is presumably 1,4 followed by rearrangement, since the 2-substituted naphthalene-1,4-dibenzenesulfonamides (IIa–IIe) are obtained.



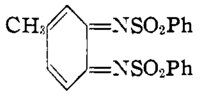
Ia, X = H
Ib, X = Cl



IIa, R = CH_3 IId, R = n-C_4H_9
IIb, R = C_2H_5 IIe, R = C_6H_5
IIc, R = n-C_3H_7



IIIa, X = SO_2Ph
IIIb, X = COPh



IV

Compounds (IIa–IIe) are obviously analogous. The constitution of the 2-ethylnaphthalene-1,4-dibenzenesulfonamide was established by an unequivocal synthesis: 2-ethyl-1-naphthylamine is treated with a diazotized solution of sulfanilic acid and the resulting azo-dye V is reduced, using stannous chloride and hydrochloric acid, to 2-ethylnaphthalene-1,4-diamine dihydrochloride (VI) which is converted to IIb by the action of benzenesulfonyl chloride in pyridine (*cf.* Scheme A).

The structure of 2-methylnaphthalene-1,4-dibenzenesulfonamide (IIa) was determined by synthesis through benzenesulfonation of 2-methylnaphthalene-1,4-diamine dihydrochloride,[4] and by comparison with a sample of this same product kindly furnished by Professor R. Adams, University of Illinois.

Excess methyl- or ethylmagnesium iodides cause decolorization of the benzene solutions of 2-chloro-1,4-naphthoquinonedibenzenesulfonimide, *p*-quinonedibenzenesulfonimide, *p*-quinonedibenzimide and 4-methyl-*o*-quinonedibenzenesulfonimide. Ap-

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[1] (a) E. Bamberger and L. Blangey (*Ann.*, **384**, 272 (1911)) studied the reaction of methylmagnesium iodide on *p*-xyloquinone, and identified hydroquinone as well as the addition products; (b) A. Fränssen (*Bull. soc. chim.*, **37**, 902 (1925); *ibid.*, **45**, 1030 (1929)) using α-naphthoquinone, isolated a di-addition product and reduction products; (c) the action of phenylmagnesium bromide on a fully substituted *p*-quinone, *e.g.*, duroquinone and 2,3-dimethyl-α-naphthoquinone, gave 1,2- and 1,4-addition products as well as reduction products (L. I. Smith and H. M. Crawford, THIS JOURNAL, **50**, 869 (1928); H. M. Crawford, *ibid.*, **57**, 2000 (1935)); (d) *cf.*, the reduction of tetrachloro- and 4-triphenylmethyl-1,2-benzoquinone by the Grignard reagents to the corresponding catechols (A. Schönberg and N. Latif, *J. Chem. Soc.*, 446 (1952)).

[2] R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950), and later papers from this Laboratory.

[3] A. Mustafa and M. Kamel, *Science*, **117**, 234 (1953).

[4] This experiment was carried out with A. Harhash.