80% ethyl alcohol, alcohol-ether, and finally with ether alone. The yield is about 0.43 g. of a purplish-black crystalline powder. The mother liquor on standing yields a further crop of dye.

We have prepared kryptocyanines also from tolulepidine ethiodide (with formaldehyde); from lepidine methiodide (with chloroform); from tolulepidine methiodide (with formaldehyde), and from tolulepidine methnitrate (with formaldehyde). The first 2 formed crystals with a characteristic reflection pleochroism; the latter 2 resembled K III in appearance. In no case was the yield as great as with K III, and none of the other dyes equaled K III in sensitizing power.

Summary.

1. A new type of photosensitizing dye having an absorption maximum near 7000 Å and a sensitization maximum near 7400 Å is described.

2. These dyes are formed by the action of alcoholic alkali and formaldehyde (or chloroform) on the alkyl halides (or other quaternary addition compounds) of (sufficiently pure) lepidine and its homologs.

3. Dyes of the same or similar type are produced under some circumstances in the absence of formaldehyde or chloroform.

4. Tentative suggestions are made as to the structure of these dyes.

5. The name "kryptocyanine" is suggested.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MISSOURI SCHOOL OF MINES.]

METHYL AMINES FROM METHYL ALCOHOL AND AMMONIUM CHLORIDE.[1]

BY W. D. TURNER AND A. M. HOWALD.

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It has been shown that ammonia can be methylated with methyl alcohol[2] by heating in an autoclave with zinc chloride as a dehydrator. The object of the present work was to determine the conditions of time; temperature, proportion of reagents, etc., best suited for the preparation of methyl amines by this reaction, and the relative importance of each factor.

Experimental Procedure.

Glass bombs were tried as a container but they failed through lack of tensile strength and through attack by the bases. We eventually found steel bombs of extra heavy 10-mm. pipe welded at one end and closed at the other with copper gasket and steel cap to be quite satisfactory. The bombs were weighed before and after charging, then after heating. In this way the loss on heating was known and this could be

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[1] An abstract of a thesis submitted by A. M. Howald, in partial fulfilment of the requirements for the degree of Master of Science at the Missouri School of Mines and Metallurgy.

[2] V. Mertz and K. Gaskioroski, *Ber.*, 17, 640 (1884).

neglected unless very large, since a complete analysis was made after heating.

Experiments were conducted at 218°, the boiling point of naphthaline, and at 303°, that of acetanilide. The bombs, charged as required, were immersed in the vapor of one of these substances and thus kept at constant temperature for definite periods. After heating the bombs were dropped into a freezing mixture, opened, and the contents washed into very dilute hydrochloric acid.

Methyl alcohol was determined as follows. The solution was distilled, using a Hoffman trap until $^1/_4$ remained. The distillate, made basic with sodium hydroxide, was again distilled and the specific gravity of this distillate determined at 15° and compared with standard tables.

Methyl amines and ammonia were determined as follows. To the original flask containing an acid solution of the bases a solution of sodium hydroxide was added in excess through a dropping funnel and the bases distilled into standard hydrochloric acid. After diluting to definite volume, an aliquot part of this distillate was titrated with standard sodium hydroxide solution, thus giving a basis for calculating the total amount of bases present and incidentally avoiding the contamination of the bulk of the sample with sodium chloride.

The 3 methyl bases and ammonia present in the bulk of the solution as their hydrochlorides were separated and estimated by the method of Berthreume,[1] the principles of which are briefly as follows: The mixed hydrochlorides evaporated and dried in a vacuum are extracted with pure dry chloroform, thus dissolving the di- and tri-amines and leaving monomethylamine and ammonia. The trimethylamine is separated from the di- by precipitating it as the tri-iodide and ammonia is separated from the monomethyl amine by precipitating it with yellow mercuric oxide in basic solution.

Results.

Ten experiments were performed with results as shown in Table I.

TABLE I.

Ratio of Mols. NH_3 = 1.

Expt.	Time hrs.	Temp. ° C.	NCH_3H_2.	$N(CH_3)_2H$.	$N(CH_3)_3$.	CH_3OH.	$ZnCl_2$.
1....	24	218	0.0154	nil.	nil.	2.97	0.00
2....	60	218	0.0290	nil.	nil.	3.05	0.00
3....	2	218	0.0792	0.0064	nil.	2.30	1.50
4....	5	218	0.055	0.012	nil.	2.17	0.00
5....	5	218	0.325	0.008	nil.	0.49	1.50
6....	5	218	0.432	0.045	0.007	5.11	1.50
7....	5	303	0.689	0.069	0.023	10.15	1.50
8....	5	303	0.098	0.015	nil.	14.04	0.00
9....	5	303	0.227	0.021	0.0034	13.57	0.75
10....	8	303	1.078	0.162	0.026	12.0	1.50

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[1] Berthreume, *Compt. rend.*, **150**, 1251 (1910).

In the first 3 experiments where ammonia was used much lower yields were obtained than in the last 7 similar experiments in which ammonium chloride was used.

Summary.

Methyl amines are formed only in traces when ammonia or ammonium chloride and methyl alcohol are heated without a dehydrator to as high as 303°.

Using zinc chloride as a dehydrator good yields of mono- and di-methylamines can be obtained. For example, in 8 hours at 303° (Expt. 10) yields were obtained as follows: monomethyl amine, 55%; dimethylamine, 7.5%; and trimethylamine, 1.86%, of the ammonium chloride used.

The yields increase with the amount of zinc chloride used, with increase in temperature, with increase in time of heating and with increase in ratio of methyl alcohol to ammonia.

In all cases where zinc chloride was used hydrogen was liberated due to the hydrolysis of the zinc chloride and consequent attack of the iron bomb by the hydrochloric acid formed. It was for this reason that no experiments could be carried to equilibrium.

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THE DECOMPOSITION OF NITRIC ACID IN ORGANIC NITRATIONS.

BY F. O. RICE.

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The decomposition of nitric acid in organic nitrations is a matter of some industrial importance because there is usually considerable reduction of nitric acid to oxides of nitrogen and if much nitrous oxide or nitrogen is formed there would be a serious loss of nitric acid. Nitric oxide and higher oxides can be reconverted into nitric acid by suitable condensing towers and returned to the system.

Some investigations[1] on the solution of metals in nitric acid have shown that at ordinary temperatures large amounts of nitrous oxide were present in the gases evolved. In many cases the metallic nitrate catalyzed the reduction of the acid to nitric oxide so that near the end of the reaction when there was much of the metal in solution almost pure nitrous oxide was obtained.

It seemed possible, therefore, that a similar reduction of nitric acid to nitrous oxide or nitrogen might take place in organic reactions. The

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[1] Acworth, *J. Chem. Soc.*, **28**, 828 (1875); Acworth and Armstrong, *ibid.*, **32**, 54 (1877); Freer and Higley, *Am. Chem. J.*, **15**, 71 (1893); Higley, *ibid.*, **17**, 18 (1895); Higley and Davis, *ibid.*, **18**, 587 (1896).