3. Up to the present, only two papers have appeared on X-ray diffraction of aqueous anisotropic phases of soaps or detergents. Ross and McBain reported that a *lamellar* structure *expanding continuously with dilution* exists both in the isotropic and anisotropic phases of the system hexanolamine oleate:water.[4] Marsden and McBain[2] found lamellar structures in the isotropic and anisotropic phases in aqueous systems of nonionic detergents, but the variation of long spacing with concentration is different for the two phases.

The aqueous liquid crystalline phase of dodecylsulfonic acid existing in the very high concentrations in the neighborhood of 85% has a *lamellar* structure, but the long spacing does *not* change with concentration. This long spacing appears to be due to the double length of the detergent molecule tilted at an angle β of about 63°. The various orders of this long spacing are in the ratio of 1:2:3 (that is, Bragg spacings in the proportion of 1: $1/\sqrt{4}$: $1/\sqrt{9}$), with no diffraction lines in between; while the side spacings consist again of halos at 7–8 Å. and 4.5–4.6 Å.

4. For comparison with the various aqueous systems just described it may be mentioned that solid dodecyl sulfonic acid exhibits long spacings corresponding to even orders of pairs of molecules of the acid placed end to end but tilted at an angle β of 55°. No diffraction corresponding to that expected for the odd orders has yet been found.

It is clear that quite different colloidal particles exist in the different concentrations and phases of aqueous dodecyl sulfonic acid. It is evident that thorough study of aqueous systems of association colloids, wherein the fundamental chemical unit is definitely known, must throw light upon the study of closely related but less well characterized systems, such as those of proteins and virus.

(4) Ross and McBain, THIS JOURNAL, **68**, 296 (1946).

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A New Method of Preparation of Diazomethane

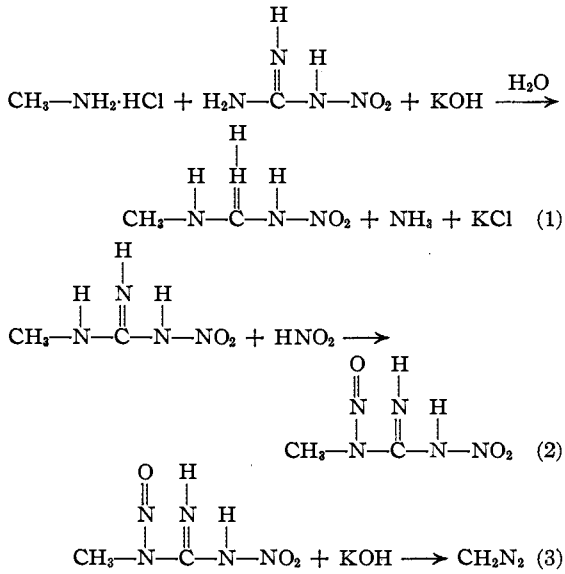
BY A. F. MCKAY

N-Methyl-N-nitroso-N′-nitroguanidine described by McKay and Wright[1] has been found to give diazomethane in 72.6% yield on reaction with aqueous potassium hydroxide.

The available methods[2] of production of diazomethane have disadvantages not encountered in the present method. The chief drawback in the method of Arndt[3] is the instability of methylnitrosourea which limits the production of this compound to 25–50 g. lots. On the other hand N-methyl-N-nitroso-N′-nitroguanidine has been prepared in pound lots and stored in the dark at room temperature for periods of time up to two months without showing signs of decomposition. N-Methyl-N-nitroso-N′-nitroguanidine changes slowly from orange to green in color on exposure to sunlight and loses nitrogen oxides. Moreover, in the purification of this compound it is best to employ an anhydrous solvent, preferably absolute methanol. Prolonged refluxing with 95% ethanol is sufficient to cause partial denitrosation with the production of N-methyl-N′-nitroguanidine.

The only disadvantage noted in handling N-methyl-N-nitroso-N′-nitroguanidine has been a skin irritation. The dermatitis is accompanied by pruritus and a burning sensation. In more severe cases a vesicant action has been noted. These skin reactions were obtained during the nitrosation of N-methyl-N′-nitroguanidine and when using the nitroso compound in other reactions. The simple expedient of performing the reactions in a fume hood eliminated these undesirable effects.

The series of reactions involved in the formation of diazomethane are



The first two reactions have been previously reported,[1] while reaction 3 is described in the experimental section. The diazomethane was characterized by methylating stearic acid. The methyl stearate obtained in quantitative yield melted at 39.0–39.5° alone and on admixture with an authentic sample.

This method is not limited to the production of diazomethane but it has been found to be of general use in the preparation of diazo compounds. The results on the broader application of this method will be published at a later date.

Experimental

Diazomethane.—The procedure used in the preparation of diazomethane from 20 g. (0.13 mole) of N-methyl-N-nitroso-N′-nitroguanidine was the same as the distillation technique described by Arndt[3] in the preparation of diazo-

(1) A. F. McKay and G. F Wright, THIS JOURNAL, **69**, 3028 (1946).
(2) L. I. Smith, *Chem. Revs.*, **23**, 193 (1938).
(3) F. Arndt, *Org. Syntheses*, **15**, 3 (1935).

methane from methylnitrosourea. The solutions in the receivers were combined and diluted to a volume of 250 cc. with anhydrous ether. A 10-cc. aliquot was used in the determination of the yield of diazomethane by the use of benzoic acid as described by Marshall and Acree.[4] The total yield was 4.15 g. or 72.6%.

Characterization of Diazomethane.—To 498 mg. (0.0017 mole) of stearic acid (m. p. 69 ± 0.1°) dissolved in 30 cc. of ether was added 331 mg. (0.0078 mole) of diazomethane in 20 cc. of ether. The ethereal solution was allowed to stand at room temperature for twenty minutes after the evolution of nitrogen had ceased. The excess diazomethane was decomposed with dilute hydrochloric acid solution and the ether fraction separated. After washing the ether solution with water (3 × 40 cc.), it was dried over anhydrous sodium sulfate and evaporated. The colorless residue crystallized on cooling. These crystals melted at 39–39.5° (capillary method) alone and on admixture with an authentic sample of methyl stearate. The yield was 514 mg. or 98.4% by theory.

Acknowledgment.—The author wishes to acknowledge the technical assistance of Mr. W. J. McIntyre.

(4) E. K. Marshall and S. F. Acree, *Ber.*, **43**, 2323 (1910).

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Volatile Decomposition Products of Sugars in Aqueous Solution

BY LOUIS SATTLER AND F. W. ZERBAN

Enders and his co-workers[1] have published a series of papers purporting to show that methylglyoxal is found in the distillate not only when alkaline solutions of glucose and xylose are distilled at constant volume, but that methylglyoxal is found in distillates of neutral and acid solutions of these sugars as well. They also report the finding of methylglyoxal in the distillates from acid solutions of sucrose, maltose, dextrin and soluble starch.

Their conclusion that methylglyoxal is indeed the volatile material in the distillate, is based upon the following observations: the iodoform reaction, the color reaction with pyrrole, the color test of Denigès,[2] as for example with codeine phosphate, the Ariyama reaction[3] with arsenophosphotungstic acid and the characterization of methylglyoxal as its phenyl and 2,4-dinitrophenylosazones.

These color reactions for methylglyoxal are not specific and the reaction with sodium nitroprusside[4] has its limitations. The isolation of the osazones is not conclusive because acetol also yields the same derivatives. Acetol makes the Ariyama test ambiguous because, as with methylglyoxal, there is a great intensification of the blue color upon the addition of sodium cyanide (1 g.). Unfortunately, the conversion of acetol into 4(5)-methylimidazole[5] does not lend itself to micro quantities.

Baudisch and Deuel[6] have shown that sugars when distilled from a 5% sodium bicarbonate solution, yield acetol. The acetol can be specifically identified[7] by its reaction with *o*-aminobenzaldehyde to form 3-hydroxyquinaldine which can be isolated. This compound crystallizes from acetone and water in the form of colorless needles melting at 260°,[8] and possesses a beautiful blue fluorescence when it is illuminated in very dilute aqueous solution with invisible ultraviolet light.

In view of Enders' claim that methylglyoxal is obtained in the distillates when maltose solutions are distilled ranging over a wide *p*H, from strongly acid to strongly alkaline,[1b] it was deemed desirable to test for acetol because of the obvious conflict of these findings with the observations of Baudisch and Deuel. Pure 20% aqueous solutions of glucose and of maltose were distilled at constant volume. The distillates gave a positive test with Ariyama's reagent, and they yielded the reported osazones. However, with *o*-aminobenzaldehyde, under the conditions described by Baudisch and Deuel,[6] the distillates gave strong positive tests for acetol as observed by fluorescence. Baudisch and Deuel found that 1 g. of methylglyoxal gives only a faint acetol test, as observed by the intensity of the fluorescence, whereas 5 mg. of glucose when distilled with a sodium bicarbonate solution, yields a relatively large amount of acetol.

Pinkus[9] obtained the osazone of methylglyoxal when glucose was treated with strong alkali in the presence of phenylhydrazine. While Nef,[10] Wohl,[11] and Neuberg[12] have expressed beliefs that in alkaline solution methylglyoxal is the initial product formed in the rupture of the sugar molecule, Baudisch and Deuel are of the opinion that acetol is the primary compound which is produced because under their experimental conditions the Cannizzaro reaction is apparently negligible. Thymine, which on treatment with ferrous sulfate and sodium bicarbonate in the presence of air, is oxidized to urea, pyruvic acid and acetol, can be detected in the presence of sugar.[6]

Our finding of acetol in the distillates of aqueous sugar solutions does not rule out the simultaneous presence of methylglyoxal. It does point up the conclusion that Enders' quantitative method for the estimation of methylglyoxal is erroneous and that his opinions regarding the formation of methylglyoxal are open to modification. Of further interest to us is the darkening of these triose solutions when they are distilled from a 5% so-

(1) (a) Enders and Marquardt, *Naturwissenschaften*, **29**, 46 (1941); (b) Enders, *Biochem. Z.*, **312**, 349 (1942); (c) Enders and Sigurdsson, *Biochem. Z.*, **317**, 26 (1944).

(2) Denigès, *Bull. soc. chim.*, **5**, 649 (1910).

(3) Ariyama, *J. Biol. Chem.*, **77**, 395 (1928).

(4) Neuberg, *Biochem. Z.*, **71**, 150 (1915).

(5) Weidenhagen and Wegener, *Z. Wirtschaftsgruppe Zuckerind.*, **88**, 927 (1938).

(6) Baudisch and Deuel, THIS JOURNAL, **44**, 1585 (1922).

(7) Baudisch, *Biochem. Z.*, **89**, 279 (1918).

(8) Königs and Stockhausen, *Ber.*, **35**, 2556 (1902).

(9) Pinkus, *ibid.*, **31**, 31 (1898).

(10) Nef, *ibid.*, **335**, 247 (1904).

(11) Wohl, *Biochem. Z.*, **5**, 57 (1907).

(12) Neuberg and Oertel, *ibid.*, **55**, 494 (1913); Neuberg and Rewald, *ibid.*, **71**, 144 (1915).