dimethoxy-9-phenanthrylamine into 3,4-dimethoxy-9-phenanthrol.[1,2] This conversion was carried out quantitatively by a modification of the Bucherer reaction wherein sulfur dioxide replaced the usual bisulfite,[4] and the presence of much aqueous dioxane prevented the formation of the diphenanthrylamine derivative. Analogous deaminations have been carried out by other methods in low or in unstated yields.[5] 3,4-Dimethoxy-9-phenanthrol gave the required 3,4,9-trimethoxyphenanthrene on methylation.

Experimental

α-Phenyl-2-nitro-3,4-dimethoxycinnamic Acid.—This was obtained in 75% yield by Pschorr's method[6] or in 90% yield by the following modification. 2-Nitroveratraldehyde, 2.1 g., phenylacetic acid, 1.4 g., triethylamine, 1.0 g., and acetic anhydride, 5 ml., were heated together at 60° for two days. Isolation and purification according to Pschorr gave the product, 3.0 g., m. p. 222.5–223.5° (uncor.).

3,4-Dimethoxy-9-aminophenanthrene.—Prepared according to Knorr,[1] the base was obtained from its hydrochloride with alcoholic potassium hydroxide.

3,4-Dimethoxy-9-phenanthrol.—3,4-Dimethoxy-9-aminophenanthrene, 4.7 g., was dissolved in 50 ml. of dioxane, 50 ml. of water added, the mixture saturated with SO_2 at 0°, and heated in a sealed tube at 100° for one day. Removal of the solvent *in vacuo*, grinding the residue with water, filtering and drying, gave 3,4-dimethoxy-9-phenanthrol, 4.7 g., m. p. 147–152°. The crude product was distilled (1×10^{-4} mm., bath temp. 130°) and crystallized from toluene, giving pale yellow prisms, m. p. 156°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; OCH_3, 24.4. Found: C, 75.53; H, 5.43; OCH_3, 21.9, 22.4.

3,4,9-Trimethoxyphenanthrene.—3,4-Dimethoxy-9-phenanthrol, 390 mg., was refluxed under nitrogen with water, 10 ml., and *N* sodium hydroxide, 2 ml. Methyl sulfate, 0.5 ml. then 0.4 ml., and *N* sodium hydroxide, 5 ml. then 4 ml., were added alternately. The cooled mixture was extracted with chloroform, the chloroform washed with dilute hydrochloric acid, with dilute sodium hydroxide with water, and dried with sodium sulfate. 3,4,9-Trimethoxyphenanthrene, 330 mg., m. p. 85–95°, was obtained by distilling (1×10^{-4} mm., bath temp. 110°) the residue left on evaporating the chloroform. It was purified by crystallizing from petrol ether (b. p. 60–80°, 20 parts) giving colorless prisms, m. p. 96.5–97.5° after drying.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; OCH_3, 34.70. Found: C, 76.21; H, 6.32; OCH_3, 31.76.

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(4) Franzen and Kempf, *Ber.*, **50**, 101 (1917).

(5) Pschorr and Schröter, *Ber.*, **35**, 2726 (1902); Schmidt and Strobel, *Ber.*, **36**, 2508 (1903).

(6) Pschorr and Sumuleanu, *Ber.*, **33**, 1810 (1900).

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X-Ray Diffraction in Aqueous Systems of Dodecyl Sulfonic Acid

BY SULLIVAN S. MARSDEN, JR., AND JAMES W. MCBAIN

Aqueous systems of lauryl sulfonic acid are especially interesting because their X-ray diffraction shows different kinds of patterns for ordinary isotropic solution, concentrated anisotropic liquid crystalline region, and the highly concentrated anisotropic liquid crystalline, and the pure crystalline acid.

1. The ordinary isotropic liquid solution existing at room temperature exhibits only a very diffuse indication of a long spacing even near the highest concentration (23%) at which it can exist. The phase diagram giving the boundaries of this[1] and the two anisotropic phases was published by M. J. Vold. X-Ray diffraction therefore indicates the absence of any strongly repeating structure such as that found in solutions of potassium laurate, except high angle scattering due to neighboring molecules in the colloidal particles of the sulfonic acid.

However, when 3.6% of benzene is added to 19.0% solution of the dodecyl sulfonic acid the solution is still isotropic but gives a diffraction line corresponding to a single order of Bragg spacing of 63.4 Å. But when the amount of benzene is increased to 6.9% the system becomes anisotropic and gives two long Bragg spacings of 67.0 Å. and 48.4 Å. It is assumed that this structure is lamellar in analogy with the system Triton X-100: water:benzene.[2]

2. Most interesting is the aqueous liquid-crystalline phase existing between 23 and 70% of lauryl sulfonic acid. The colloidal particles apparently consist of *fibers* or long rods or elongated ellipsoids. These lie parallel at a distance from each other in hexagonal arrangement. Such a structure was found for certain aqueous systems of tobacco mosaic virus by Bernal and Fankuchen.[3]

The evidence for this interpretation of the X-ray diffraction patterns follows from: (a) The ratios of the successive Bragg spacings to each other are in the proportions $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$. These correspond to hexagonal indices $10\bar{1}0$, $11\bar{2}0$, $20\bar{2}0$, $21\bar{3}0$, respectively.

(b) Most important, the relative intensities of the various diffractions, which in the order given above are: very strong, strong, weak and very weak, respectively; in a few cases the second and third lines are strong and strong, respectively.

(c) The variation of the inter-particle distance with concentration, which is approximately as the reciprocal of the square root of the concentration.

The thickness or diameter of the fibers seems to be in the neighborhood of the double length of the soap molecule. The short spacings consist of halos at 7–8 Å. and 4.5–4.6 Å., which indicates a liquid arrangement of neighboring molecules within the fibers.

It should be mentioned that this structure is quite different from that of the anisotropic phases of aqueous potassium laurate as is shown by studies in this laboratory by Oscar A. Hoffman being reported elsewhere. He shows that the potassium laurate systems contain a repeating *lamellar* structure such as was first suggested by Hess and his collaborators.

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(1) Vold, THIS JOURNAL, **63**, 1427 (1941).

(2) Marsden and McBain, *J. Phys. & Coll. Chem.*, **52**, 110 (1948).

(3) Bernal and Fankuchen, *J. Gen. Physiol.*, **25**, 111 (1941).

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

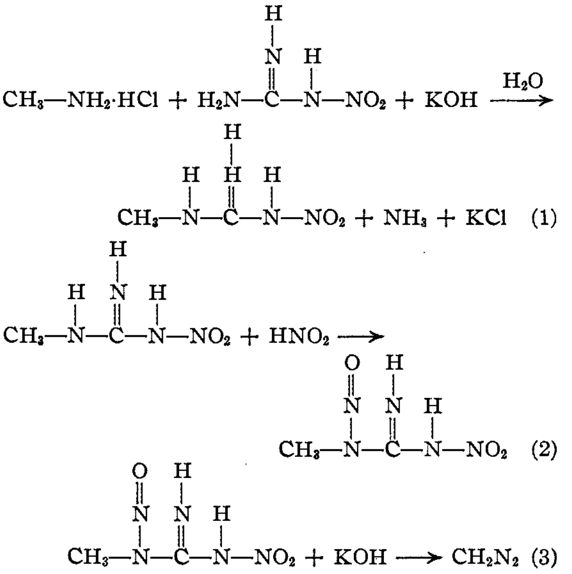
By A. F. McKay

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



$$CH_3-NH_2\cdot HCl + H_2N-\overset{\overset{H}{|}}{\overset{N}{\overset{\|}{C}}}-\overset{H}{\overset{|}{N}}-NO_2 + KOH \xrightarrow{H_2O} CH_3-\overset{H}{\overset{|}{N}}-\overset{\overset{H}{|}}{\overset{H}{\overset{\|}{C}}}-\overset{H}{\overset{|}{N}}-NO_2 + NH_3 + KCl \quad (1)$$

$$CH_3-\overset{H}{\overset{|}{N}}-\overset{\overset{H}{|}}{\overset{N}{\overset{\|}{C}}}-\overset{H}{\overset{|}{N}}-NO_2 + HNO_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{\overset{N}{\overset{|}{N}}}-\overset{\overset{H}{|}}{\overset{N}{\overset{\|}{C}}}-\overset{H}{\overset{|}{N}}-NO_2 \quad (2)$$

$$CH_3-\overset{\overset{O}{\|}}{\overset{N}{\overset{|}{N}}}-\overset{\overset{H}{|}}{\overset{N}{\overset{\|}{C}}}-\overset{H}{\overset{|}{N}}-NO_2 + KOH \longrightarrow CH_2N_2 \quad (3)$$

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-

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[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).