hydrous sodium sulfate, poured back into the distilling flask and the crude epichlorohydrin thus freed from water fractionated again. After a small forerun the pure epichlorohydrin distilled at 30–32° under 10 mm. pressure; the yield was 770 g. of epichlorohydrin or 80% of the theoretical. The epichlorohydrin thus obtained boiled at 115–117° and had a specific gravity of 1.18 at 20°.

(b) **Epibromohydrin.**—One liter (2140 g.) of dibromohydrin was suspended in 1.5 liters of water and then gradually under shaking 420 g. of calcium hydroxide was added in the course of fifteen minutes. Then 420 g. of calcium hydroxide was added at once and the epibromohydrin distilled under reduced pressure in the same manner as is described in the case of epichlorohydrin. The united lower layers of two distillations (690 + 70 = 760 cc.) were fractionated under 50 mm. pressure and the medium fraction, after drying with anhydrous sodium sulfate, fractionated again. The yield of epibromohydrin (b. p. 61–62° under 50 mm. pressure or 134–136° at ordinary pressure) was 1200 g. or 90% of the theoretical. The product had a specific gravity of 1.665.

CONTRIBUTION FROM   GÉZA BRAUN
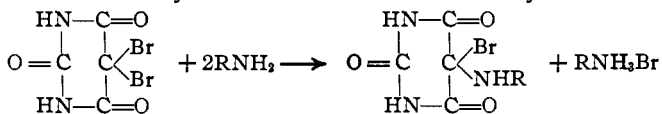THE FLEISCHMANN LABORATORIES
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COMMUNICATIONS TO THE EDITOR

THE REACTION OF DIBROMOBARBITURIC ACID WITH AMINES

Sir:

In a recent communication Nightingale and Schaefer[1] describe the reaction of 5,5-dibromobarbituric acid with primary and secondary amines. The reaction is said to yield a series of 5-bromo-7-alkyl uramils.

Such a reaction seems improbable in view of the general properties of the class of "persubstituted" halogen compounds.[2] Such compounds act as brominating agents, the active halogen being replaced by hydrogen. To quote a single example, bromonitromalonic ester reacts with dimethylamine to form the amine salt of nitromalonic ester and N-bromodimethylamine.[3] Baeyer[4] and Biltz and Hamburger[5] obtained the ammonium

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[1] Nightingale and Schaefer, THIS JOURNAL, **54**, 236 (1932).

[2] *Cf.* a summary by Schmidt, Ascherl and von Knilling, *Ber.*, **59**, 1876 (1926), which includes over seventy references to the literature.
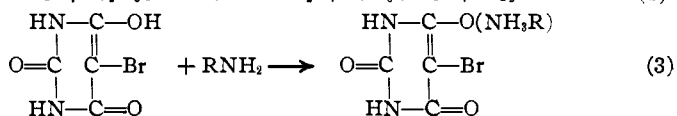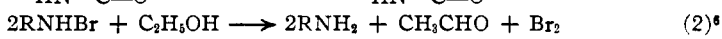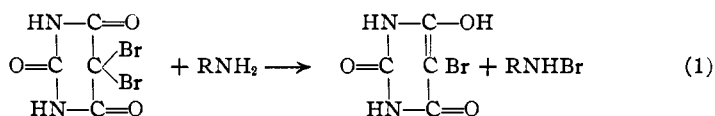
[3] Willstätter and Hottenroth, *Ber.*, **37**, 1776 (1904).

[4] A. Baeyer, *Ann.*, **130**, 134 (1864).

[5] Biltz and Hamburger, *Ber.*, **49**, 641 (1916).

salt of monobromobarbituric acid on treating dibromobarbituric acid with aqueous ammonia.

From a consideration of the above evidence it seemed probable that the compounds reported by Nightingale and Schaefer were not 5-bromo-7-alkyl uramils, but merely the amine salts of 5-bromobarbituric acid. The authors mention the fact that their products are decomposed by alkalies with the liberation of the amine. This would be a very unusual reaction for a substituted uramil, since uramil itself is hydrolyzed slowly by alkalies into urea and aminomalonic acid. The liberation of the amine would be expected, however, on treating alkyl ammonium 5-bromobarbiturates with alkali. These salts lack but two hydrogen atoms of being isomeric with the uramils; consequently the nitrogen and bromine analyses which constitute the only proof of structure offered by Nightingale and Schaefer could be explained by either formula. From results reported[3] in the literature it would seem that the formation of these salts could be accounted for by the reactions

$$\begin{array}{c} HN-C=O \\ | \quad | \quad /Br \\ O=C \quad C< \\ | \quad | \quad \backslash Br \\ HN-C=O \end{array} + RNH_2 \longrightarrow \begin{array}{c} HN-C-OH \\ | \quad || \\ O=C \quad C\ Br \\ | \quad | \\ HN-C=O \end{array} + RNHBr \qquad (1)$$

$$2RNHBr + C_2H_5OH \longrightarrow 2RNH_2 + CH_3CHO + Br_2 \qquad (2)^6$$

$$\begin{array}{c} HN-C-OH \\ | \quad || \\ O=C \quad C-Br \\ | \quad | \\ HN-C=O \end{array} + RNH_2 \longrightarrow \begin{array}{c} HN-C-O(NH_3R) \\ | \quad || \\ O=C \quad C-Br \\ | \quad | \\ HN-C=O \end{array} \qquad (3)$$

In order to establish the structure of the compounds prepared by Nightingale and Schaefer their work was repeated with ethylamine, di-n-propylamine and di-n-amylamine. The products agreed in physical properties with those which they reported, and all of them were decomposed immediately by cold 10% sodium hydroxide with the liberation of the amine. Such a rapid reaction is characteristic of the liberation of an amine from a salt, and not of the splitting of a nitrogen to carbon linkage. The reaction was carried out quantitatively in one case. The di-n-propylamine salt (1 g.) was treated with an excess of cold 20% sodium hydroxide and the free amine extracted with ether. The amine was extracted from the ether solution with dilute hydrochloric acid, the extract being placed in a Kjeldahl apparatus and made alkaline with 20% sodium hydroxide. The amine was determined by distillation into an excess of standard acid: required, 32.47 cc. of 0.1 N sulfuric acid, or 100.03% calcd. The titrated solution was evaporated to dryness and dipropylamine dipropyldithiocarbamate prepared as a derivative; m. p. 118–118.5°, mixed with a known

⁶ Reaction 2 is not essential to the formation of the salts, but merely indicates the method by which the amine is regenerated; *cf.* Biltz and Behrens, *Ber.*, **43**, 1984 (1910); Berg, *Ann. chim.*, (7) **3**, 339 (1894).

specimen gave no depression. Monobromobarbituric acid was obtained from each of the salts by a procedure similar to that employed by Biltz and Hamburger[5] with the ammonium salt. Yields of 30–50% of pure 5-bromobarbituric acid were obtained; m. p. 215–216°;[7] Br calcd., 38.61; found, 38.90. The loss is due to the solubility of the sodium salt and the instability of 5-bromobarbituric acid in aqueous solution.[7]

The products obtained by Nightingale and Schaefer have thus been demonstrated to be alkyl ammonium 5-bromobarbiturates. The "dark tarry oils" which they obtained with dibromobarbituric acid and aromatic amines were formed in a similar bromination process; such experiments have been reported previously in the literature. Dibromobarbituric acid and aniline give monobromobarbituric acid and p-bromoaniline,[8] while with dimethylaniline monobromobarbituric acid and p-bromodimethyl-aniline are obtained.[9]

[7] Bock, Ber., 55, 3401 (1922).

[8] Conrad and Reinbach, ibid., 35, 522 (1902).

[9] Gupta and Thorpe, J. Chem. Soc., 121, 1898 (1922).

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CESIUM FILMS ON TUNGSTEN

Sir:

When cesium atoms strike a tungsten filament at high temperature (filament surrounded by negatively charged cylinder), every atom is ionized. At lower temperature the number of adsorbed atoms (adatoms) per unit area (σ) can be measured by flashing the filament and allowing the evaporated atoms to strike a second parallel filament from which they evaporate as ions. The potentials of the two filaments are so chosen that no ions escape from the first but all escape from the second. A galvanometer ballistic kick gives a quantitative determination of σ.

Dr. J. Bradshaw Taylor has developed this method for measuring the rates of evaporation of atoms (ν_a), ions (ν_p) and electrons (ν_e) as functions of σ and T. The following conclusions are drawn.

The tungsten surface, after considerable heating at 2800°K., is homogeneous, except that a small fraction (0.0050) can hold adatoms more firmly than the rest. With rising pressure, and a filament at 1100–1200°K., the first atoms are adsorbed on this active surface, which becomes saturated before 0.5% of the remaining surface is occupied. The active spots are separate spaces holding one atom each from which the heat of evaporation is 80 Kg. cal. per g. atom. The following refers to the homogeneous surface.