tals (0.6 g.) separated, m.p. 260–262° with decomposition. The ferric chloride reaction in alcohol gave a brown color turning red after a few minutes.

Anal. Calcd. for $C_{12}H_7NO_6$: C, 55.2; H, 2.7; N, 5.3. Found: C, 54.9; H, 2.9; N, 5.2.

2-Methyl-5-hydroxy-8-aminofuro-4′,5′-6,7-chromone (IIb).—(IIa), 1.0 g., 30 ml. of hydrochloric acid (sp. gr. 1.18) and 5.0 g. of tin (added gradually) were heated with continual stirring on a boiling water-bath until all the tin went into solution (about two hours). Twenty ml. of distilled water was then added, the solution boiled for about one minute and filtered hot (sintered glass filter). The deep yellow filtrate was cooled, left overnight in the ice-chest and then filtered. The yellow, crystalline precipitate of the tin hydrochloride complex of (IIb), which melted at about 245° with strong evolution of gas, was dissolved in 20 ml. of distilled water, 10 ml. of a 20% solution of sodium acetate was then added, followed by the gradual addition of 10% aqueous sodium hydroxide, until the *p*H of the solution was adjusted between 6.5 and 7.0. (IIb) came down as a cream colored crystalline precipitate, which was filtered off. Recrystallized from acetone the product gave 0.5 g. of yellowish crystals which melted at 225°.

Anal. Calcd. for $C_{12}H_9NO_4$: C, 62.3; H, 3.9; N, 6.1. Found: C, 62.6; H, 3.8; N, 6.4.

2-Methyl-furo-4′,5′-6,7-chromone-5,8-quinone (III).—(IIb), 1.0 g., was dissolved in a hot mixture of 5 ml. of sulfuric acid (sp. gr. 1.8) and 30 ml. of distilled water. After cooling to room temperature, the mixture was treated drop by drop (continuous stirring) with a solution of 2.0 g. of sodium dichromate in 20 ml. of distilled water, then left to stand at room temperature for about one hour and filtered. Recrystallized from acetone the product weighed 0.3 g. and melted at about 239° with decomposition.

(III) gives no color reaction with ferric chloride; it dissolves in sulfuric acid (sp. gr. 1.8) with an orange color and in 10% aqueous sodium hydroxide to give a violet solution.

Anal. Calcd. for $C_{12}H_6O_5$: C, 62.6; H, 2.6. Found: C, 63.1; H, 2.6.

2-Methyl-5,8-dihydroxyfuro-4′,5′-6,7-chromone (IVa).—(III), 1.0 g., was dissolved in 20 ml. of a 10% sodium bisulfite solution, and the mixture treated at room temperature with 2 ml. of hydrochloric acid, and then heated on the water-bath to free it completely of sulfur dioxide. The mixture was cooled and filtered; the yellow crystalline product obtained weighed 0.8 g. and melted at 278°. This was identical with the product obtained from khellin by demethylation.[1]

Anal. Calcd. for $C_{12}H_8O_5$: C, 62.1; H, 3.4. Found: C, 62.0; H, 3.7.

2-Methyl-5,8-dimethoxyfuro-4′,5′-6,7-chromone (IVb) (Khellin).—A mixture of (IVa), 1.0 g., 100 ml. of acetone, 6.0 g. of potassium carbonate and 5 ml. of methyl iodide was refluxed for 24 hours, then cooled and filtered. The potassium salts were washed twice with hot acetone, and the washings added to the main acetone solution. The acetone was evaporated, the residue boiled with 300 ml. of water and the aqueous solution filtered hot. On cooling 0.5 g. of almost colorless needles was obtained, which when recrystallized from alcohol melted at 153–154° and proved to be khellin by a mixed melting point determination and the color reaction with potassium hydroxide pellets.

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.6; H, 4.6. Found: C, 64.9; H, 4.4.

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(1) Schönberg and Aly Sina, This Journal, **72**, 3398 (1950).

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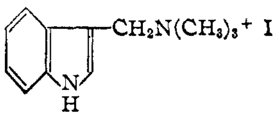
Gramine Methiodide

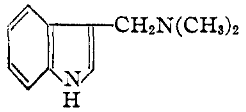
BY CHARLES H. SCHRAMM[1]

During the course of an investigation involving the synthesis of certain indole derivatives, it was necessary to prepare gramine methiodide (I).



I

Kühn and Stein[2] obtained this compound by adding methyl iodide to an alcoholic solution of gramine (II), and reported that the product, in a melting point determination, turned brown at 175° but did not melt when heated to 350°. Snyder[3] used the procedure of Kühn and Stein but did not report a melting point for their methiodide. Wieland and Hsing[4] prepared the same compound in methanol solution and reported similar results, but they expressed some doubt concerning the identity of their product in light of the work of Orechoff and Norkina.[5] These latter authors claimed a melting point of 176–177° for gramine methiodide prepared in ethanol from the alkaloid Donaxin. On the other hand, Wieland and Hsing, although suspecting a case of dimorphism, did not find it possible to prepare the 176–177° product. No attempt has been made to reconcile these results.



II

It has been found possible to obtain both methiodides depending upon the reaction conditions used. When gramine reacted with methyl iodide in cold absolute *ethanol*, the methiodide melting at 172–173° was obtained and this was found to be a metastable or "labile" modification. The reaction of the same gramine with methyl iodide in *methanol* solution yielded the "stable," non-melting isomer. When the low-melting product was recrystallized from ethanol, the stable isomer was obtained. No change in melting point (172–173°) was observed when the labile isomer was recrystallized from methanol. It was not possible to convert the stable modification into the metastable one. Both compounds behaved in identical fashion in subsequent reactions.

Experimental

Gramine.—This compound was prepared according to the method of Kühn and Stein.[2]

Gramine Methiodide. Metastable Isomer.—Forty grams of gramine was dissolved in 280 cc. of absolute ethanol. This represented an almost saturated solution. The alcoholic solution was stirred with a mechanical stirrer, and 37.8 g. of methyl iodide was added over a period of one-half hour. Cold water was used to control the reaction during this addition. Crystals of the methiodide separated within a short time. It was thereby possible to obtain 62.6 g. (86%) of pure white needles, m.p. 172–173°. Recrystallization from methanol did not change the melting point.

Gramine Methiodide. Stable Isomer.—A solution of 1.0 g. of gramine in 5 cc. of methanol was treated with 0.8 g. of methyl iodide. The methiodide (1.6 g.) crystallized almost immediately. In a melting point determination, this mate-

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(1) Research Department, Lever Brothers Company, Cambridge, Mass.

(2) H. Kühn and O. Stein, *Ber.*, **70**, 567 (1937).

(3) H. R. Snyder, C. W. Smith and J. M. Stewart, This Journal, **66**, 200 (1944).

(4) T. Wieland and C. Y. Hsing, *Ann.*, **526**, 188 (1936).

(5) A. Orechoff and S. Norkina, *Ber.*, **68**, 436 (1935).

rial behaved in a manner analogous to the product synthesized by Kühn and Stein.

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The Reduction of Certain Halogenated Nitroparaffins by Liquid Ammonia. II. Brompicrin

BY EDWARD SCHULZ, SEYMOUR MEISEL AND FREDERIC C. SCHMIDT

Schmidt, Sunderlin and Cole[1] showed that dibromodinitromethane, dichlorodinitromethane and chlorobromodinitromethane are reduced by anhydrous ammonia at its boiling point with the loss of a halogen according to the general equation

$$3X_2C(NO_2)_2 + 8NH_3 \longrightarrow 3XC(NO_2)_2NH_4 + 3NH_4X + N_2$$

When bromochlorodinitromethane was used, it was the bromine which was removed.

Hsing-Han Liu and Peter P. T. Sah[2] attempted to prepare guanidine from tribromonitromethane and alcoholic ammonia, but reported that the reaction mixture exploded.

This investigation shows the reaction of tribromonitromethane (brompicrin) with anhydrous liquid ammonia and a possible mechanism for the reaction.

Experimental

Preparation of Materials. Brompicrin.—Brompicrin was obtained from Eastman Kodak Co. and steam distilled. The product was dried over anhydrous sodium sulfate, vacuum distilled and collected over a temperature range of 85–87° (16 mm.); $d^{20}{}_4$ 2.7880; n_D 1.5790; m.p. 10.2–10.3°.

Dibromomononitromethane.—The method of Scholl was used except in the purification of the material. The dibromonitromethane obtained reacted with anhydrous liquid ammonia to give the ammonia salt. The salt was dissolved in distilled water, reforming the dibromonitromethane by the addition of an excess of hydrobromic acid; b.p. 53–54° at 17 mm. pressure; $d^{20}{}_4$ 2.3846; n_D 1.528.

Reaction of Brompicrin with Anhydrous Liquid Ammonia.—A fragile bulb filled with a weighed amount of brompicrin was placed in a reaction vessel which was kept at −33° by a dewar filled with liquid ammonia. The vessel was evacuated, and about 50 ml. of liquid ammonia was distilled into it. The bulb was broken by means of a plunger. A violent reaction occurred between the brompicrin and the ammonia accompanied by a colorless inert gas. The evolved gas was washed free from ammonia and dried overnight over phosphorus pentoxide. After drying, the gas was drawn into an evacuated flask of known volume and the density determined. The molecular weight of the contained inert gas was calculated to be 28; 28.5 for two different determinations. This is in excellent agreement with the molecular weight of nitrogen, 28. The ratio of the moles of brompicrin to moles of nitrogen formed is given in Table I.

TABLE I

QUANTITATIVE REDUCTION OF BROMPICRIN

Grams	Moles $\times 10^{-3}$	N_2 liberated moles $\times 10^{-3}$	$BrC(NO_3)/N_2$
1.4214	4.77	1.62	2.94:1
2.2549	7.85	2.49	3.05:1

After the nitrogen had been completely evolved, the excess liquid ammonia was allowed to evaporate leaving a bright yellow solid. This solid, suspected of being a mixture of the ammonium salt of dibromonitromethane and ammonium bromide, was treated with an excess of aqueous HBr. The heavy oil which separated was washed with water, dried and vacuum distilled: $d^{20}{}_4$ 2.3845; n_D 1.528. These physical constants are identical with those of dibromonitromethane. The infrared spectrum of this oil was compared to that of known dibromonitromethane and they were found identical.

The other solid, beside the ammonium salt of dibromonitromethane, was shown by analysis to be ammonium bromide in equal molar quantities.

Discussion of Results.—The evidence of Table I along with the infrared spectra determinations, density and index of refraction measurements indicates without doubt that the reaction between brompicrin and anhydrous liquid ammonia proceeds according to the equation

$$3Br_3CNO_2 + 8NH_3 \longrightarrow 3BrCNO_2NH_4 + 3NH_4Br + N_2$$

This equation is similar to that found by Schmidt, Sunderlin and Cole[1] for dibromodinitromethane.

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RECEIVED FEBRUARY 26, 1951

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[1] Schmidt, Sunderlin and Cole, *J. Org. Chem.*, **9**, 419 (1944).

[2] Hsing-Han Liu and Peter P. T. Sah, Science Reports, National Tsinghua University, A_2 129-B1 (1933).

A New Synthesis of Glyoxal Tetramethyl Acetal

BY RALPH C. SCHREYER

Glyoxal tetramethyl acetal has been prepared from glyoxal sulfate and methanol[1] or glyoxal sulfate, methanol and calcium chloride.[2] Acetals of glyoxal have also been synthesized from aqueous glyoxal and alcohols.[3]

Recently in this Laboratory the preparation of glyoxal tetramethyl acetal has been accomplished by the addition of chlorine to 1,2-dimethoxyethylene[4] followed by reaction with methanol.

$$CH_3OCH{=}CHOCH_3 + Cl_2 \longrightarrow CH_3OCHClCHClOCH_3$$
$$+ 2CH_3OH \longrightarrow (CH_3O)_2CHCH(OCH_3)_2 + 2HCl$$

Attempts to isolate the chlorine addition product by vacuum distillation were unsuccessful because of dehydrochlorination of the reactive bis-chloroether.

In most cases, it was desirable to add some sodium methoxide after the reaction with methanol in order to drive the reaction to completion and to remove all traces of hydrogen chloride. Higher yields would probably be attained if a stoichiometric amount of sodium methoxide were employed instead of using methanol. This synthesis should be applicable to other 1,2-dialkyloxyethylenes, allowing the synthesis of other acetals or mixed acetals of glyoxal.

Experimental

Glyoxal Tetramethyl Acetal.—Chlorine (24 g., 0.34 mole) was added slowly over a 15-minute period to 30 g. (0.34 mole) of 1,2-dimethoxyethylene stirred at 0°. A white solid separated out from the reaction mixture. Methanol (22 g., 0.69 mole) was then added at 0° and the resulting solution was heated to 60° until the evolution of hydrogen chloride ceased (time about one-half hour). Vacuum dis-

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[1] H. O. L. Fischer and C. Taube, *Ber.*, **59B**, 851 (1926).

[2] D. H. Grangaard and C. B. Purves, THIS JOURNAL, **61**, 428 (1939).

[3] L. G. MacDowell and R. W. McNamee, U. S. Patent 2,321,094 (1943); U. S. Patent 2,360,959 (1944).

[4] Dimethoxyethylene is prepared by the demethanolation of 1,1,2-trimethoxyethane, W. F. Gresham, U. S. Patent 2,479,068; 1,1,2-trimethoxyethane is synthesized from (1) carbon monoxide, hydrogen, methanol and methylal using a cobalt catalyst, W. F. Gresham and R. E. Brooks, U. S. Patent 2,449,470, or (2) methanol and methoxyacetaldehyde.