Summary

Benzil-disodium, $C_6H_5C(ONa)=(NaO)CC_6H_5$, is formed in quantitative yield by the action of 2% sodium amalgam on benzil in a mixture of ether and benzene at room temperature. Anisil, 4,4'-diphenylbenzil and α-naphthil yield disodium derivatives under similar conditions. This reaction offers a convenient method of obtaining these compounds and from them derivatives of dihydroxystilbene, $C_6H_5C(OH)=(HO)CC_6H_5$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Preparation of Dibromoamine and its Reaction with Grignard Reagents

BY GEORGE H. COLEMAN, CHARLES B. YAGER AND HAROLD SOROOS

Monobromoamine[1] has been prepared in this Laboratory by a modification of the method of Moldenhauer and Burger.[2] The first attempts to adapt the method to the preparation of ethereal solutions of monobromoamine led to products in which the bromine to nitrogen ratio was considerably greater than 1.0. This suggested the possibility that dibromoamine was also formed. The formation of the two compounds can be represented by the equations

$$2NH_3 + Br_2 \longrightarrow NH_2Br + NH_4Br \qquad (1)$$

$$3NH_3 + 2Br_2 \longrightarrow NHBr_2 + 2NH_4Br \qquad (2)$$

By changing the manner in which the bromine and ammonia were brought together from that used in the preparation of monobromoamine and by changing the relative quantities used, ethereal solutions of dibromoamine have been prepared in which the bromine to nitrogen ratio was approximately 2.0. That the 2.0 ratio is not due to a mixture of monobromoamine and bromine is shown by the following considerations. The amber color of the solution of dibromoamine is distinctly different from the color of a solution containing enough free bromine to produce a ratio of bromine to nitrogen of 2.0. When ammonia is passed into a cold dibromoamine solution, no precipitate of ammonium bromide is formed. Such a precipitate would be formed immediately if free bromine were present.

Both monobromoamine and dibromoamine are unstable at 0° and are best prepared at temperatures obtainable with solid carbon dioxide. The rates of decomposition of the two compounds in ethereal solution at 0 and −72° are shown in Fig. 1. Dibromoamine is less stable at 0° than monobromoamine but rather anomalously can be prepared in greater concentration than monobromoamine. In Fig. 2 are shown the rates of decomposition of dibromoamine at 0 and −72° in ethereal solution of the higher concentration usually obtained. Attempts to prepare monobromoamine solutions of this concentration were not successful.

The reaction of dibromoamine was studied with nine Grignard reagents which were also used with monobromoamine. The results are given in Table I.

TABLE I

PERCENTAGE YIELDS OF AMINES, AMMONIA AND NITROGEN FROM DIBROMOAMINE AND GRIGNARD REAGENTS

Reagents	RNH_2	R_2NH	NH_3	N_2	Total
n-C_4H_9—Mg—Cl	15	5	70	7	97
n-C_4H_9—Mg—Br	5	1	89	..	95
n-C_4H_9—Mg—I	2	0.4	95	1	98
s-C_4H_9—Mg—Cl	21	5	62	8	96
t-C_4H_9—Mg—Cl	24	5	53	9	91
t-C_4H_9—Mg—Br	16	5	67	4	92
t-C_4H_9—Mg—I	3	1	89	7	100
C_6H_5—CH_2—Mg—Cl	34	6	41	4	85
$C_6H_5C_2H_4$—Mg—Cl	18	3	73	1	95

The percentage yields are calculated on the basis of the nitrogen content of the dibromoamine solutions. An excess of the Grignard reagent was always used. The reactions may be represented by equations similar to those given for the reaction of monobromoamine[1] with Grignard reagents. The yields of primary amines are less than those obtained with monobromoamine. The yields of secondary amines are much less than the yields of primary amines, a result which might be expected from a consideration of the reaction of alkyldichloroamines[3] with Grignard reagents. The variation in yields of amines with reagents prepared from chlorides, bromides and iodides which is characteristic of monochloroamine and monobromoamine was observed in this work.

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[1] Coleman, Soroos and Yager, THIS JOURNAL, **55**, 2075 (1933).

[2] Moldenhauer and Burger, *Ber.*, **62**, 1615 (1929).

[3] Coleman, THIS JOURNAL, **55**, 3001 (1933).

Experimental

Preparation of Dibromoamine.—About 500 cc. of dry ether was placed in a tube of 700 cc. capacity and cooled to −50° by placing the tube in a Dewar flask containing a mixture of solid carbon dioxide and acetone. Ten cubic centimeters of bromine was added to the cold ether and dry ammonia was passed slowly into the solution until the red color of the solution turned to yellow. The addition of ammonia was continued for a few minutes in order to provide a slight excess.

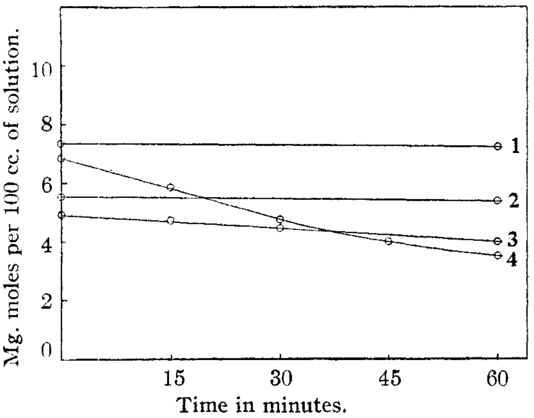

Fig. 1.—Decomposition rates of monobromoamine and dibromoamine: 1, $NHBr_2$ at −72°; 2, NH_2Br at −72°; 3, NH_2Br at 0°; 4, $NHBr_2$ at 0°.

The apparatus and the method used to separate the ammonium bromide and excess ammonia from the ether solution are described under the preparation of monobromoamine.[1] The ether solution of dibromoamine was collected in a cold graduated tube and cooled to −70° to cause the separation of water in the form of ice. Ethereal solutions prepared by this method were pale amber in color and contained from 40 to 50 mg. moles in 350 cc. of solution.

Analysis of Dibromoamine Solution.—The method of analysis was the same as that described for monobromoamine solutions. The results of several determinations showed that the bromine to nitrogen ratio was usually between 1.98 and 2.05.

Decomposition Rates of Mono- and Dibromoamine Solutions.—An ethereal solution of dibromoamine was prepared in the usual manner and cooled to −72°. Half of this solution was transferred by means of a vacuum-jacketed tube to a tube immersed in an ice-bath at zero degrees. Samples for analysis were withdrawn from the solution in the ice-bath as soon as possible and again when the solution had reached the temperature of the bath. The temperature of the solution at the time the first sample was taken was −5°. About fifteen minutes was required for the temperature of the solution to rise to 0°. Samples were withdrawn at fifteen-minute intervals for one hour. Samples were also withdrawn from the solution maintained at −72°, but in this case at the end of one, two and five hours. The results are shown by the curves in Fig. 2. The decomposition at −72° was so much slower than at 0° that only two experimental points are included on the curves at −72° in Figs. 1 and 2. The values determined at the end of two and five hours were found to lie on the same straight line.

The rate of decomposition of an ethereal solution of monobromoamine was determined in the same way. In order to compare the rate of decomposition of dibromoamine in a solution of approximately the same concentration as the monobromoamine solution, dibromoamine was prepared in the usual way and diluted with about an equal volume of cold ether before determining the decomposition rate. The results for both monobromoamine and the diluted solution of dibromoamine are shown in Fig. 1.

Reaction of Dibromoamine with Grignard Reagents.—The apparatus used and the methods of carrying out the reaction and isolating the products were essentially those used with monobromoamine.

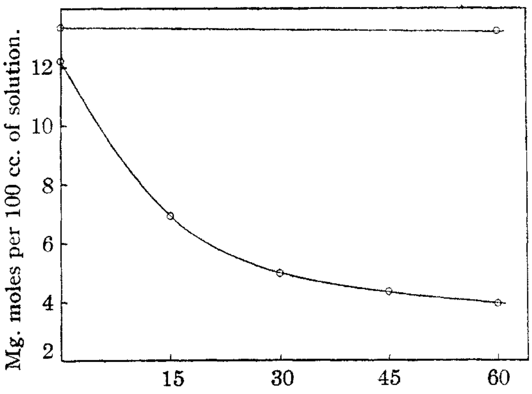

Fig. 2.—Decomposition rates of dibromoamine: upper curve, $NHBr_2$ at −72°; lower curve, $NHBr_2$ at 0°.

Separation of the Amine Mixtures.—After separation of the amine hydrochlorides from ammonium chloride, the primary and secondary amines were separated by the modification of Hinsberg's method described in the paper on alkylchloroamines.[3] In addition to the separation of amines by this method, the mixture of amines obtained in the reaction of dibromoamine with benzylmagnesium chloride was separated by fractional distillation. The dibenzylamine was identified by the preparation of suitable derivatives.

Summary

Dibromoamine has been prepared in ethereal solution.

At zero degrees dibromoamine is less stable than monobromoamine. Both monobromoamine and dibromoamine are relatively stable at −72°.

Dibromoamine reacts with Grignard reagents to form primary amines, secondary amines, ammonia and nitrogen.

Iowa City, Iowa

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