

yielded 14 g. of  $\beta$ -chloroethanesulfonyl chloride. Hydrolysis yielded  $\beta$ -chloroethanesulfonic acid.<sup>10</sup>

**Ammonium  $\beta$ -Chloroethanesulfonate.**—The viscous  $\beta$ -chloroethanesulfonic acid was treated with concd. ammonium hydroxide and the solution evaporated to dryness under reduced pressure. The residue was crystallized from alcohol.

*Anal.* Calcd. for  $C_2H_5O_3ClNS$ : C, 14.86; H, 4.99. Found: C, 15.18; H, 5.25.

**Taurine** was prepared by heating ammonium  $\beta$ -chloroethanesulfonate for twelve hours in a sealed tube at 105° with an excess of concd. ammonium hydroxide. Upon cooling, taurine separated out. It was recrystallized several times from water and was identical with a sample of taurine prepared by the method of Marvel, Bailey and Sparberg.<sup>7</sup> Identity was established by means of crystallographic examination.<sup>11</sup>

**Potassium  $\beta$ -Hydroxyethanesulfonate from Taurine.**—Acetic acid was added slowly to a hot aqueous solution

(10) Kohler, *Am. Chem. J.*, **20**, 683 (1898).

(11) We are indebted to Dr. E. B. Sandell of the Division of Analytical Chemistry for the crystallographic comparisons reported in this paper.

containing taurine and potassium nitrite. After no further gas evolution, addition of acetic acid was discontinued and the solution was evaporated to dryness. The solid residue was extracted with hot alcohol. The alcohol extract yielded crystalline potassium  $\beta$ -hydroxyethanesulfonate; m. p. 189–191°.

*Anal.* Calcd. for  $C_2H_5O_4SK$ : K, 23.80. Found: K, 23.84.

A crystallographic examination showed this product to be identical with the one obtained by the addition of potassium bisulfite to ethylene oxide. Attempts to convert sodium  $\beta$ -bromoethanesulfonate to sodium  $\beta$ -hydroxyethanesulfonate by means of silver oxide led to products which were unsuited for crystallographic comparison.

### Summary

The addition compound obtained by the action of sodium or potassium bisulfite on ethylene oxide has been shown to possess the  $\beta$ -hydroxysulfonic acid structure, a result which was generally accepted, but not demonstrated previously.

MINNEAPOLIS, MINN.

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

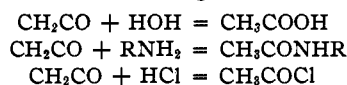
## The Reaction of Haloamines with Ketenes

BY GEORGE H. COLEMAN, ROLF L. PETERSON AND GILBERT E. GOHEEN

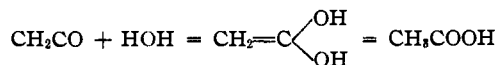
Previous work in this Laboratory has shown that in the addition of nitrogen trichloride to unsaturated compounds<sup>1</sup> a chlorine atom in nitrogen trichloride behaves as though it were electropositive with respect to the  $NC\ell_2$  group. By analogy it might be assumed that the halogens in other haloamines such as monochloroamine, monobromoamine, dibromoamine and the alkylchloroamines would show a similar behavior. The reactions of these compounds with reducing agents support this assumption. Attempts to bring about addition reactions of some of the haloamines other than nitrogen trichloride with unsaturated hydrocarbons have not been thus far successful. Monochloroamine reacts with Grignard reagents<sup>2</sup> to form primary amines and ammonia. With many of these reagents the percentage of amine formed is much greater than the percentage of ammonia. Such a result does not seem to be consistent with the assumption that in all reactions the  $NH_2$  group in monochloro-

amine is electronegative with respect to the chlorine.

In the present work a study was made of the reactions of monochloroamine, dibromoamine, nitrogen trichloride and dimethylchloroamine with ketene and diphenylketene. The suitability of ketenes for this work depends on the fact that they are very reactive substances which add diverse molecules in a definite manner, as illustrated in the following well-known examples



The activity of this class of compounds may be due to addition to the carbonyl group first and then rearrangement of the resulting enol form as postulated by Staudinger,<sup>3</sup> *e. g.*



Regardless of the mechanism, however, by which the addition takes place, the final product is such that the electropositive portion of the adding molecule is found attached to the carbon farthest

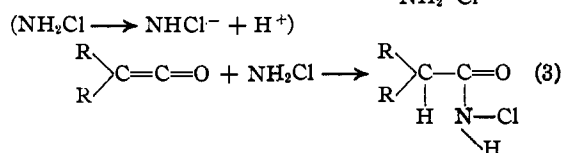
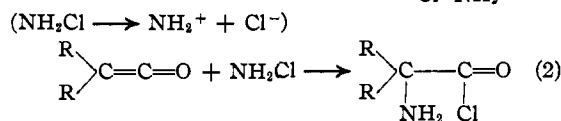
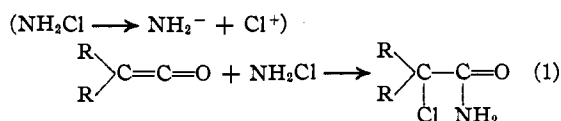
(1) Coleman and co-workers, *THIS JOURNAL*, **45**, 3084 (1923); **49**, 2593 (1927); **50**, 1816 (1928); **50**, 2739 (1928); **50**, 2754 (1928); **51**, 937 (1929).

(2) (a) Coleman and Hauser, *ibid.*, **50**, 1193 (1928); (b) Coleman and Yager, *ibid.*, **51**, 567 (1929); (c) Coleman and Forrester, *ibid.*, **58**, 27 (1936).

(3) Schlenk and Bergmann, "Ausführliches Lehrbuch der organischen Chemie," Franz Deuticke, Vienna, 1932, Vol. I, p. 374.

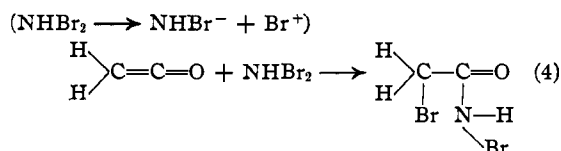
from the oxygen and the electronegative portion to the carbon to which the oxygen is united.

Applying these considerations to the question of the character of the halogen atoms in haloamines the following possibilities can be formulated for the reaction of monochloroamine with ketenes



Diphenylketene was found to react with monochloroamine to form diphenylchloroacetamide according to equation (1). No evidence of the formation of other addition products was observed although the yield of diphenylchloroacetamide isolated was only 51% of the theoretical. With unsubstituted ketene ( $\text{CH}_2\text{CO}$ ) N-chloroacetamide was formed in 70–75% yields, the reaction apparently occurring according to equation (3). The fact that the reaction with diphenylketene proceeds differently than that with ketene is not necessarily surprising, considering the electronegative character of the phenyl groups relative to hydrogen (Kharasch).<sup>4</sup>

Dibromoamine and ketene formed monobromoacetamide, a result most readily explained by assuming the reaction



The replacement of the bromine on nitrogen by hydrogen is probably due to the presence of hydrobromic acid in the reaction mixture. If dibromoamine added to ketene in any other manner, acetamide or glycine would be the final product under the experimental conditions. It also seems quite improbable that the bromine on carbon could be due to direct bromination.

(4) (a) Kharasch and Flenner, *THIS JOURNAL*, **54**, 674 (1932);  
(b) Kharasch, *J. Chem. Education*, **8**, 1703 (1931).

A nearly quantitative yield of N,N-dimethyldiphenylchloroacetamide was formed in the reaction of dimethylchloroamine with diphenylketene. In the light of previous work this product was to be expected.

With ketene and dimethylchloroamine a liquid product was obtained which after distillation had a chlorine and nitrogen content corresponding to that of N,N-dimethylchloroacetamide.

Nitrogen trichloride reacted with ketene to give as a final product monochloroacetamide in about 14% yields. This is in agreement with the assumption of relatively electropositive chlorine atoms in nitrogen trichloride. Boismenu<sup>5</sup> states that N,N-dichloroacetamide is unstable above 0°, decomposing with the liberation of chlorine. This instability may account in part for the low yield. The substitution of hydrogen for the chlorine on nitrogen is again doubtless due to the formation of hydrochloric acid in the reaction mixture.

The reaction of nitrogen trichloride with diphenylketene has been reported previously.<sup>6</sup> The results were interpreted as indicating the formation of N,N-dichlorodiphenylchloroacetamide which was transformed to benzophenone-imide hydrochloride. This reaction was repeated under different experimental conditions and a product isolated which was unstable at room temperature and contained chlorine attached to nitrogen. Its chlorine content corresponded to that of N,N-dichlorodiphenylchloroacetamide.

### Experimental

**Preparation of Haloamines.**—The methods used in the preparation and analysis of monochloroamine,<sup>2c,7</sup> dibromoamine,<sup>7</sup> dimethylchloroamine<sup>8</sup> and nitrogen trichloride<sup>9</sup> were essentially those which have been described previously.

**Preparation of Diphenylketene.**—Diphenylketene was prepared as described by Schroeter.<sup>10</sup> The method has been investigated more recently by Ritter and Wiedeman.<sup>11</sup> It consists in the oxidation of benzil monohydrazone in benzene solution with yellow mercuric oxide. The azibenzil which is formed loses nitrogen on heating and rearranges to the ketene. The observations of Ritter and Wiedeman with respect to the freshness and character of the mercuric oxide to be used were substantiated. It was noticed that the tendency to form the side product bisbenzalketazine increased whenever the concentration of

(5) Boismenu, *Ann. chim.*, [9] **9**, 166 (1918).

(6) Coleman and Campbell, *THIS JOURNAL*, **50**, 2754 (1928).

(7) Coleman, Yager and Soroos, *ibid.*, **56**, 965 (1934).

(8) Coleman, *ibid.*, **55**, 3001 (1933).

(9) Coleman, Buchanan and Paxson, *ibid.*, **55**, 3669 (1933).

(10) Schroeter, *Ber.*, **42**, 2346 (1909).

(11) Ritter and Wiedeman, *THIS JOURNAL*, **51**, 3583 (1929).

TABLE I

Reactants	Yield, %	M. p., °C.	Formula of product	Analyses, %			
				Calcd.		Found	
				N	Cl	N	Cl
CH <sub>2</sub> CO + NH <sub>2</sub> Cl	73	111-112	CH <sub>2</sub> CONHCl	14.96	37.96	14.85	37.86
CH <sub>2</sub> CO + NHBr <sub>2</sub>	18	88-89	CH <sub>2</sub> BrCONH <sub>2</sub>		Br, 57.93		Br, 57.99
CH <sub>2</sub> CO + NCl <sub>3</sub>	14	114-115	CH <sub>2</sub> CICONH <sub>2</sub>				
CH <sub>2</sub> CO + (CH <sub>3</sub> ) <sub>2</sub> NCl		B. p. 98-100° (11 mm.)	CH <sub>2</sub> CICON(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	11.53	29.20	11.57	29.05
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCO + NH <sub>2</sub> Cl	51	116-117	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCICONH <sub>2</sub>		14.44		14.41
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCO + NCl <sub>3</sub>		112 <sup>b</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCICONCl <sub>2</sub> <sup>a</sup>		33.9		35.08
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCO + (CH <sub>3</sub> ) <sub>2</sub> NCl	95	122-123	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CCICON(CH <sub>3</sub> ) <sub>2</sub>				

<sup>a</sup> Not completely identified. <sup>b</sup> Copper block method.

the azibenzil solution was too great or whenever the solution was allowed to stand for some time. This was accompanied by premature slow evolution of nitrogen. The formation of the side product was avoided by using 8-9 cc. of dry benzene per gram of benzil monohydrazone, keeping the temperature at 23-24° during the oxidation and working up the reaction mixture without extended delay. In a typical run using 90 g. of powdered benzil monohydrazone there was obtained 44 g. of diphenylketene, b. p. 120-124° (1 mm.). This was 56% of the theoretical yield.

**Preparation of Ketene.**—Ketene was prepared by the method described by Hurd.<sup>12</sup> It was collected by bubbling the gases from the condenser into anhydrous ether cooled to -60°. The concentration was determined by adding aliquot portions to 3.5 *N* alkali and titrating the excess alkali with standard acid. The ethereal solutions were used at once.

The general method of carrying out the reactions with the haloamines is typified in the procedures described for the reactions of monochloroamine with ketene and diphenylketene. The essential results of the seven reactions studied are given in Table I. The products, with the exception of the two noted in the table, were identified by comparison with authentic samples.

**Monochloroamine with Ketene.**—Two hundred and twenty cubic centimeters of an ethereal solution containing 0.12 mole of monochloroamine was cooled to -60° and added to 225 cc. of an ethereal solution containing 0.162 mole of ketene also at -60°. The solutions were not exposed to moist air, the addition of the monochloroamine solution being effected through a vacuum jacketed glass tube. A white turbidity appeared at once. The reaction

mixture was kept at -60° for three hours and then allowed to warm to room temperature and filtered. The white precipitate weighed 2.60 g. The filtrate was partially evaporated and a second crop of white crystals weighing 4.56 g. obtained. By complete evaporation of the solvent a third portion was obtained which after purification weighed 1.06 g. The total product weighed 8.22 g. It was recrystallized by dissolving in warm ether and cooling the solution to about -60°. Shiny white plates were formed, m. p. 111-112°.

**Monochloroamine with Diphenylketene.**—This reaction was carried out in a manner similar to that used with ketene. An ethereal solution of 0.13 mole of monochloroamine was added at -65° to an ethereal solution of 0.106 mole of diphenylketene. As the monochloroamine was added the orange color of the ketene solution faded and a white precipitate formed which proved to be ammonium chloride. The mixture was kept at -60° for thirty minutes, then allowed to warm to room temperature and kept at this temperature for eight hours. It was then filtered and the solvent evaporated at room temperature or below under reduced pressure. The residue was recrystallized from toluene. The total weight of material obtained melting above 105° was 13.4 g. (51% of the theoretical yield). After further recrystallization the product melted at 116.5-117°.

### Summary

The haloamines monochloroamine, dibromoamine, nitrogen trichloride, and dimethylchloroamine react with ketene and diphenylketene to form amides or halogen substituted amides.

(12) Hurd, "Organic Syntheses," Coll. Vol. I, 1932, p. 324.