Following the 1-hr. reaction period the pyridine salt was filtered off directly and washed with petroleum ether. The ethyl ether was not removed from the reaction mixture because of the relatively low solubility of diethylmalonic anhydride in pure petroleum ether. As a result, the product (7.6 g., 85%) obtained by evaporation of the filtrate contained a trace of pyridine salt, but this did not seem to affect pyrolysis of the anhydride seriously.

However, cyclic anhydrides containing substantial amounts of pyridine salt (as when pure ethyl ether was used as solvent) gave only traces of the ketenes upon pyrolysis. The ability of tertiary amine salts to catalyze dimerization of ketenes has been noted before.[14]

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.12; H, 7.09; mol. wt., 142. Found: C, 58.52; H, 7.15; mol. wt., 144.

Dibutylketene.—Six grams of dibutylmalonic anhydride in a 50-ml. flask was pyrolyzed by heating at < 0.2 mm. pressure in the previously described semimicro distillation apparatus. Decomposition began at a pot temperature of about 140°; this was gradually increased to 180°, causing the ketene to distil. The entire pyrolysis took about 20 min., and gave 4.0 g. of dibutylketene (85% based on cyclic anhydride) with $n^{20}_{\rm D}$ 1.4312.

The product is of near analytical purity but sometimes contains a trace of fluorine compounds (infrared absorption at 1230, 1176, and 1103 cm.$^{-1}$) which may be removed by redistillation if desired. Pure dibutylketene is a yellow liquid with b.p. 68–69° (10.5 mm.), 75–76° (15 mm.), $n^{20}_{\rm D}$ 1.4308, d^{20} 0.831.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.89; H, 11.76. Found: C, 77.72; H, 11.90.

Comparable yields were obtained with smaller (1.7 g.) and larger (9 g.) amounts of cyclic anhydride.

Diethylketene.—Because of its volatility, diethylmalonic anhydride was pyrolyzed at atmospheric pressure in a slow stream of nitrogen. A 7.6-g. quantity was brought to 120° in 10 min., then gradually heated to 170° over the next 20 min. Although monomeric, this anhydride seemed to pyrolyze more slowly than the dibutyl anhydride. The diethylketene produced weighed 2.9 g. (56%); its infrared curve showed no carbonyl bands and only traces of fluorine compounds. Its $n^{20}_{\rm D}$ was 1.4126 (lit.[15] value 1.4112).

Ethylphenylketene was best prepared by the pyrolysis of ethylphenylmalonyl trifluoroacetate: To 10 g. (0.0480 mole) of ethylphenylmalonic acid in 65 ml. of ether was added 14.15 ml. (0.1 mole) of trifluoroacetic anhydride. After standing for 5 min. the mixture was evaporated at 2 mm. pressure for 1.5 hr. at room temperature, giving 18.2 g. (94%) of ethylphenylmalonyl trifluoroacetate with infrared carbonyl absorption at 1850 and 1780 cm.$^{-1}$.

Pyrolysis of the mixed anhydride was conducted at 15 to 20 mm. pressure and 140–160° temperature over a 20-min. period. The receiver was cooled with ordinary ice in order to trap only the ketene and not the trifluoroacetic anhydride presumably formed. The crude product (6.6 g.) had weak carbonyl bands at 1850, 1808, and 1780 cm.$^{-1}$ due to impurities which could only partially be separated from the ketene by fractionation through a 10-cm. Vigreux column.

The product was assayed for the ketene by treating with dry methanol, evaporating the excess methanol, and subjecting the residue to vapor phase chromatography. The area of the methyl 2-phenylbutyrate peak was then compared with a calibration curve prepared from an authentic sample of this ester and showed the crude product to contain 80% ethylphenylketene (the actual yield of the ketene was thus 0.8 × 6.6 g., or 5.3 g. (75%).

The chromatograms showed only two major impurities to be present, and neither formed methyl 2-phenylbutyrate upon reaction with methanol.

Infrared Spectra of Anhydride Mixtures.—Almost immediately after addition of trifluoroacetic anhydride (in a 1:1 molar ratio) to an ethereal solution of phenyl-, amyl-, or ethylphenylmalonic acid, an infrared band appeared in the ketene region of the spectrum (2200–2100 cm.$^{-1}$), then gradually diminished. The band was at 2140 cm.$^{-1}$ for the monosubstituted acids and 2130 cm.$^{-1}$ for ethylphenylmalonic acid. With a 2:1 molar ratio of anhydride to acid the band was much more intense for the monosubstituted acids but did not appear for ethylphenylmalonic acid.

Acknowledgment.—The author wishes to thank Dr. Lester P. Kuhn for many helpful discussions concerning the course of this work and the writing of this article.

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An Investigation of the Hofmann Reaction of Perhaloacetamides

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Reactions of trichloroacetamide with aqueous sodium hypobromite (Hofmann conditions) gave variable yields of cyanate (73–80%), bromotrichloromethane (34–53%), ammonia (4.5–6.8%), and chloroform (<0.5%); whereas the decomposition of N-bromotrichloroacetamide with sodium hydroxide solution gave reproducible yields of cyanate (88%), bromotrichloromethane (56%), ammonia (4.4%), and chloroform (<0.5%). The reaction of N-bromotribromoacetamide with aqueous sodium hydroxide gave cyanate (74%), carbon tetrabromide (39%), ammonia (24%), and bromoform (3.4%). The results are compared with those reported for the Hofmann reaction of trifluoroacetamide and are interpreted in terms of three simultaneous reaction paths: hydrolysis of the amide, a normal Hofmann reaction to give the trihalomethylamine, and an abnormal Hofmann reaction to give bromotrihalomethane.

In a reinvestigation of the Hofmann reaction of trifluoroacetamide, Barr and Haszeldine[2] found that bromotrifluoromethane and ammonia were the only volatile products; hexafluoroethane, previously reported[3] to be the product, was not found.

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[1] Abstracted from the Ph.D. dissertation of Donald D. Wilson, University of Kentucky, December, 1960.

[2] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 30 (1957).

[3] E. Gryszkiewicz-Trochimowski, A. Sporzynski, and J. Wnuk, *Rec. trav. chim.*, **66**, 426 (1947).

TABLE I

EFFECT OF INCREASING BASE CONCENTRATION AND THE ADDITION OF SODIUM HALIDE ON THE DECOMPOSITION OF N-BROMOTRICHLOROACETAMIDE

Conditions		Products[a]								
Mole ratio, NaOH/amide	Mole ratio, NaX/amide	NH_3, %	NCO^-, %	Cl^-, %	Br^-, %	$BrCCl_3$, %	$CHCl_3$, %	CCl_2Br_2, %	CCl_2BrH, %	CCl_4, %
2.0	...	32[b]	0[c]	21	56	42	12	0.1	0.2	0.2
3.6	...	4	88	36	42	56	0.5	.0	.0	.1
3.6	1.0(Br)	6	86	..	..	54	0.4	.3	.1	.1[d]
3.6	1.0(Cl)	6	80	38	47	48	1.7	.1	.1	.1[d]
12.8	...	9	78	45	46	50	0.6	.0	.0	.5

[a] Small amounts of hexachloroethane were formed in all experiments. [b] Represents evolved ammonia only. [c] In an identical experiment 3.2% cyanate was found. [d] Liquid product contained 1.3% hexachloroethane.

The bromotrifluoromethane could be obtained in yields of 10–35% and was accompanied by corresponding yields of cyanate. The remainder of the starting material was accounted for as sodium perfluoracetate. Earlier, Husted and Kohlhase[4] found that bromotrifluoromethane was formed when *N*-bromotrifluoroacetamide was heated with sodium hydroxide.

The Hofmann reaction of trichloroacetamide has been reported by Hine and Rosscup[5] to result in the formation of bromotrichloromethane.

The formation of cyanate and halogen substituted compounds, or hydrolysis products thereof, has been observed in other experiments where substituted amides were subjected to Hofmann conditions. Some of the substances reported to react in this way are α-monochloro amides,[6] α-monobromo amides,[6] benzoylformamide,[7] α-hydroxy amides,[8,9] α-methoxy amides,[9] and α-nitroacetamide[10] (cyanate not determined).

The purpose of this research was to determine the extent to which the anomalous Hofmann reaction occurs with trichloroacetamide and tribromoacetamide and to correlate the nature of the halogen in the amide molecule with the reaction path followed.

Results

The reaction of trichloroacetamide with alkaline sodium hypobromite under optimum conditions produced cyanate (80%), bromotrichloromethane (53%), ammonia (4.5%), and chloroform (0.5%). In a second experiment, using identical conditions, the yields were cyanate (73%), bromotrichloromethane (34%), ammonia (6.8%), and chloroform (0.17%).

The decomposition of N-bromotrichloroacetamide in sodium hydroxide solution of the same concentration (3.6 moles of sodium hydroxide per mole of amide) used in the hypobromite reactions gave yields of major products which were reproducible to ±1–2%. The effect of varying the initial base concentration on the yields of these products as well as the effect of adding sodium halide to the reaction mixture was determined. The results are listed in Table I.

The yields of products obtained from the decomposition of N-bromotribromoacetamide in sodium hydroxide solution were determined and compared with the yields obtained from the N-bromotrichloroacetamide reaction and with those reported[2] for trifluoroacetamide. These data are summarized in Table II.

TABLE II

EFFECT OF NATURE OF HALOGEN ON THE DECOMPOSITION OF N-BROMOTRIHALOACETAMIDES IN SODIUM HYDROXIDE

CX_3-CONHBr, X	NH_3, %	NCO^-, %	$BrCX_3$, %	HCX_3, %
F[a]	90–65[b]	10–35	10–35	...
Cl	4.5	88	56	0.5
Br	24	74	39	3.5

[a] Reaction products from CF_3CONH_2 and NaOBr, ref. 2. [b] Sodium trifluoroacetate also formed in 90–65% yield.

Discussion

Attempts to obtain reproducible yields of products from the reaction of trichloroacetamide with sodium hypobromite were unsuccessful. Since the decomposition of N-bromotrichloroacetamide with alkali did provide reproducible yields, it is concluded that the yield fluctuations are due to the instability of hypobromite solutions.[11] Accordingly, the reactions reported herein involve the decomposition of N-bromoperhaloacetamides with base.

N-Bromotrichloroacetamide may react with base to form the anion or it may undergo hydrolysis to the amide. The amide, in turn, may be converted into the acid and ammonia. The ammonia produced, then, may be regarded as evidence of this hydrolysis. The cyanate present in the reaction mixture does not significantly contribute to the ammonia yield since only a maximum of 7% is hydrolyzed under the reaction conditions.

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(5) J. Hine and R. J. Rosscup, *ibid.*, **82**, 6117 (1960).

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The decarboxylation of sodium trichloroacetate to give chloroform[12] and the decomposition of chloroform to dichlorocarbene[13] provide a reasonable explanation for the formation of the minor products: chloroform, bromodichloromethane, dibromochloromethane, and carbon tetrachloride. That this idea is correct is confirmed by the observation that the quantities of these minor products are less than the quantity of ammonia produced and that ammonia, chloroform, bromodichloromethane, dibromochloromethane, and carbon tetrachloride are formed when trichloroacetamide reacts with sodium hydroxide and sodium bromide solution.

The major products—cyanate and bromotrichloromethane—probably arise from the decomposition of the anion of N-bromotrichloroacetamide. There is a possibility that the bromotrichloromethane may have been produced from the reaction of sodium trichloroacetate with sodium hypobromite, a reaction analogous to the Hunsdiecker reaction.[14] Since only 1% of bromotrichloromethane was obtained from an experiment using these reactants, the contribution of this reaction path is negligible. It is also unlikely that the bromotrichloromethane arose from a bimolecular reaction of bromide on trichloroacetamide, since bromotrichloromethane was not formed during the hydrolysis of trichloroacetamide in the presence of sodium hydroxide and sodium bromide.

In previous reports[2,6a,7] of the abnormal Hofmann reaction in other systems, the organic halogen compound formed in the reaction, or its hydrolysis product, was accompanied by an equivalent yield of cyanate ion. In the experiments reported here, the cyanate ion yield varied with the base concentration of the reaction medium.

At the lower base concentration, the absence or decrease in yield of cyanate is probably due to an increase in the decomposition of cyanate in the medium to form urea and ammonium carbonate[15] (or ammonia). The presence of ammonia, from the hydrolysis of trichloroacetamide, in the reaction mixture would tend to increase the quantity of urea formed. In addition, the hypobromous acid, formed in the hydrolysis of the N-bromo amide, could decompose cyanate to form nitrogen in the same way that hypochlorous acid decomposes cyanate.[16]

In those experiments in which N-bromotrichloroacetamide and N-bromotribromoacetamide were decomposed in the stronger alkaline solutions, the yields of cyanate ion were consistently and significantly larger than the yields of bromotrihalomethane.

The most reasonable explanation of this observation is that the normal Hofmann reaction occurred forming trihalomethylamines which decompose spontaneously. Barr and Haszeldine[17] found that perfluoroalkylamines are readily dehydrohalogenated to nitriles in media of high dielectric constant. By analogy, trichloromethylamine (and tribromomethylamine) may be expected to undergo dehydrohalogenation to the corresponding nitrile, chlorocyanogen (and bromocyanogen), which has been reported[18] to decompose in basic solutions to chloride and cyanate ions. Support for this reaction path is derived from the observation that the yield

$$CCl_3NH_2 + 2OH^- \longrightarrow ClCN + 2Cl^- + 2H_2O$$

$$2OH^- + Cl{-}CN \longrightarrow Cl^- + NCO^- + H_2O$$

of chloride ion corresponds to that expected from the fraction of molecules undergoing the normal Hofmann reaction. Although Ascher[19] reported the synthesis of trichloromethylamine from trichloroacetamide, the compound could not be isolated in the experiments reported here. Hine and Rosscup[5] also could not isolate trichloromethylamine.

Cyanate ion is not produced by attack of hydroxide ion on the amide anion since its yield (relative to that of bromotrichloromethane) did not increase with increasing base concentration.

The major products of the reaction appear to arise when the anion of N-bromotrichloroacetamide undergoes either a normal Hofmann rearrangement to form the amine or an abnormal Hofmann rearrangement to form the halogen compound.

It can be assumed that the portion of molecules undergoing the normal Hofmann reaction follow the generally accepted mechanism[20] for the Hofmann rearrangement. A radical mechanism for the abnormal Hofmann rearrangement can be excluded if it is assumed that the reaction in the trihalo amide series proceeds by the same path as that observed in the α-chloro amide series. The experiments of Munk and Stevens[21] on the stereospecificity of the mechanism indicate that the radical mechanism is of minor importance.

Stevens[6a] suggested either an ionic S$_N$2 or an S$_N$i mechanism for the abnormal Hofmann rearrangement of α-bromo amides and Barr and Haszeldine[2] suggested an S$_N$i mechanism for the perfluoro amides. In the case of N-bromotrichloroacetamide an S$_N$2 reaction is unlikely because the addition of sodium bromide to the reaction mixture failed to increase the yield of bromotrichloromethane and the addition of sodium chloride failed to

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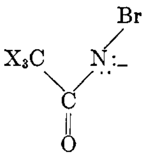
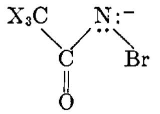
[21] M. E. Munk and C. L. Stevens, Abstracts, 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept. 1959, p. 53-P.

increase the yield of carbon tetrachloride. Radioactive bromine exchange experiments with N-bromochloroisobutyramide[22] also exclude a bimolecular mechanism for the abnormal Hofmann reaction.

The fraction of molecules which undergo the abnormal Hofmann rearrangement will depend upon the magnitude of positive charge on the α-carbon atom and on the relative concentrations of conformers I and II.


I


II

X = F, Cl, Br

Conformer I on reaction would give bromotrihalomethane and cyanate while II would yield the trihalomethyl isocyanate and bromide.

If it is assumed that bromotrichloromethane arises primarily from the abnormal Hofmann rearrangement, that cyanate arises from a combination of normal and abnormal Hofmann rearrangements, and that bromide arises from the normal Hofmann rearrangement and from the hydrolysis of the N-bromo amide, it is possible to estimate the portion of N-bromo amide undergoing the normal Hofmann reaction, the abnormal Hofmann reaction, and hydrolysis. Such an estimate, including the effects of the halogen substituent, base concentration, and halogen concentration on the reaction path followed is summarized in Table III.

TABLE III

REACTION PATHS FOLLOWED BY N-BROMOTRIHALOACETAMIDE

X	Mole ratio, NaOH–amide	Normal Hofmann rearrangement, %	Abnormal Hofmann rearrangement, %	Hydrolysis to amide, %
Cl	3.6	32	56	10
Cl	3.6[a]	32	48	15
Cl	12.8	28	50	18
Br	3.6	35	39	26
F[b]	...	0	10–35	65–90

[a] Contains 1.0 mole sodium chloride. [b] Ref. 2.

The addition of halide or an increase in the base concentration increased the extent of hydrolysis of the N-bromo amide probably by removing the N-substituted bromine atom as a positive ion and resulting in the formation of hypohalous acid or a dihalogen compound.

$$Cl_3CCONHBr + X^- \longrightarrow Cl_3CCONH^- + XBr$$

From the data presented in Table III, it appears that the effect of the nature of the halogen on the reaction path followed is the result of opposing inductive and resonance effects and that, therefore, no definite support for a given mechanism can be derived from the influence of the halogen atom.

Experimental[23]

Trichloroacetamide.—Crude trichloroacetamide was obtained in 85–90% yield by the method of McBee, Pierce, and Bolt[24] and was purified by sublimation, m.p. 140–140.5° (lit. m.p. 141[25]).

N-Bromotrichloroacetamide.—The method used was essentially that of Park, Gerjovich, Lycan, and Lacher[26] except that a glacial acetic acid solvent was used instead of trifluoroacetic acid. From 45.5 g. (0.28 mole) of trichloroacetamide 49.9 g. (74%) of N-bromotrichloroacetamide was obtained. After recrystallization from carbon tetrachloride, the sample melted at 123.5–124.5° (lit. m.p. 124–125°[2]). An assay[27] indicated that the product was 99% N-bromo amide.

Tribromoacetamide.—The use of the procedure of Broche[28] produced, after recrystallization from water, a 68% yield of tribromoacetamide, m.p. 120.5–121.5° (lit. m.p. 121–122°[29]).

N-Bromotribromoacetamide.—Application of the method previously described for the preparation of N-bromotrichloroacetamide was used. The crude product on recrystallization from carbon tetrachloride gave a 30% yield of N-bromotribromoacetamide melting at 125–127°. On analysis,[27] the product was found to be 93.5% N-bromo amide.

Analytical Methods.—The products of the Hofmann reactions were separated by steam distillation. The volatile products were collected in a Barrett trap and the nonvolatile residue, upon completion of the distillation, was diluted to a standard volume.

Nonvolatile Products.—Qualitative tests were carried out on the residue for cyanide,[30] formate,[31] cyanate,[32] and oxalate[33]. Bromide was determined quantitatively by the of Lane.[34] Chloride was found by subtracting bromide from method the total halogen measured by the Volhard method. Cyanate was determined as the dicarbamylhydrazine.[2] A calibration curve prepared from standard cyanate solutions was used to obtain the cyanate concentration in the residue.

Ammonia.—Ammonia was determined by a standard titrimetric procedure.

Volatile Liquid Product.—The volatile water-insoluble product obtained from the Barrett trap was dried over magnesium sulfate and the dry weight determined and analyzed by gas chromatography using a 2-meter column packed with Celite impregnated with Dow Corning Silicone oil 200. Calibration curves were used to obtain the weight per cent of the products.

Reactions of the Perhalo Compounds. Reaction of Trichloroacetamide Using the Method of Ascher.[19]—The reaction of trichloroacetamide with sodium hypobromite as described by Ascher yielded only impure starting material.

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[22] M. E. Munk, R. D. Elliott, and C. L. Stevens, Abstracts 139th Meeting of the American Chemical Society, St. Louis, Missouri, March, 1961, p. 33-O.

[23] All melting points were taken on a Fisher-Johns melting point block and are corrected. Boiling points are uncorrected.

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The aqueous reaction mixture contained cyanate but not cyanide, formate, or oxalate.

Apparatus.—The apparatus used in the experiments involving the perhaloacetamides and N-bromoperhaloacetamides is that described herein except for variations in the size of the reaction vessel. A three-necked round-bottom flask was equipped with a gastight stirrer, a gas inlet tube, a thermometer, and a 16-in. Vigreux column. Connected to the top of the Vigreux column was a Barrett trap and condenser which in turn was joined to a series of traps; the first contained a 4% boric acid solution, and the second was cooled in a Dry Ice–acetone mixture.

Reaction of Trichloroacetamide with Sodium Hypobromite (Hofmann Conditions).—To a mixture of 32.5 g. (0.2 mole) of trichloroacetamide and 38.4 g. (0.24 mole) of bromine which had been stirred for 10 min. at 0° a cold solution of 48.0 g. (1.2 moles) of sodium hydroxide in 240 ml. of water was added slowly until the mixture turned a bright yellow. The ice bath was removed, the solution stirred for 30 min., and the remaining sodium hydroxide solution, warmed to 60°, added to the reaction mixture. The reaction mixture was stirred for 25 min. in an oil bath heated to 60° and then, with nitrogen passing through the system heated rapidly to reflux (104°) conditions. After 9 min., distillation of the volatile product began and was complete in 16 min. After an additional 25-min. heating period, the reaction mixture was cooled and the volume adjusted to 500 ml. A small amount of white solid had collected in the condenser. Both the residue and the volatile products were analyzed; consistent analyses were not obtained from duplicate experiments. Results from representative experiments are recorded in the results section. Oxalate, cyanide, and formate were not detected in the residue.

Isolation of N-Bromotrichloroacetamide.—In another experiment, the reaction was interrupted after 30 min. by the addition of glacial acetic acid and sodium chloride. The mixture was extracted with warm carbon tetrachloride and the extract cooled. A crystalline product which contained 8.8% N-bromo amide was obtained.

Hydrolysis of Trichloroacetamide with Sodium Hydroxide and Sodium Bromide.—The procedure used was similar to that described for the reaction of trichloroacetamide with sodium hypobromite. From 16.2 g. (0.1 mole) of trichloroacetamide, 16.0 g. (0.4 mole) of sodium hydroxide, and 10.3 g. (0.1 mole) of sodium bromide there was obtained 98.4% ammonia, 11.6% chloroform, and 1.0% bromodichloromethane. Cyanate was not found in the residue.

Reaction of Trichloroacetic Acid with Alkaline Hypobromite Solution.—A solution of 32.8 g. (0.2 mole) of trichloroacetic acid in 40 ml. of water was neutralized with 20% sodium hydroxide, and added to a cold solution of 38.4 g. (0.24 mole) bromine and 20% sodium hydroxide. The mixture was subjected to the Hofmann conditions. In 16 min., the oil product began to distil and after 35 min. the reaction was quenched by cooling in an ice–salt bath. The reaction mixture was acidified and extracted with twelve 25-ml. portions of ether, the extract dried, and the ether removed by distillation under reduced pressure. Titration of the residue with standard sodium hydroxide indicated a recovery of 28% of trichloroacetic acid. Neither oxalate nor formate was detected in the residue. From the oil, there was obtained 1% bromotrichloromethane, 33% chloroform, 3% bromodichloromethane, and 0.3% dibromodichloromethane.

Reaction of N-Bromotrichloroacetamide with Sodium Hydroxide (Hofmann Conditions).—A mixture of 14.4 g. (0.36 mole) of sodium hydroxide, 24.3 g. (0.1 mole) of N-bromotrichloroacetamide, and 120 ml. of water was stirred for 25 min. in an oil bath at 60°. Then, with nitrogen flowing through the system, it was heated rapidly to reflux (104°). After 8 min. the water-insoluble volatile products began to distill and distillation was complete in 16 min. Refluxing was continued for a total of 25 min. and the reaction mixture was cooled in an ice bath. The aqueous residue and the volatile product were analyzed. Results of a representative experiment are reported in Table I under the mole ratio of sodium hydroxide–amide equal to 3.6. A small amount of white solid, m.p. 185–186°, appeared in the condenser during the reaction. The melting point of a mixture of this substance and hexachloroethane was 185–186°.

When 2 moles of sodium hydroxide per mole of amide was used, a different product distribution was obtained (see Table I). The pH of the reaction mixture at the completion of the reaction was 8.

In another experiment in which 0.1 mole of sodium hydroxide was used, trichloroacetamide (49%) and bromine were the only products isolated. Cyanate was not detected in the reaction mixture.

The results of an experiment in which the hydrolysis was carried out with a higher concentration of sodium hydroxide are recorded in Table I.

Reaction of N-Bromotrichloroacetamide with Sodium Hydroxide in the Presence of Sodium Halide.—The procedure and conditions were identical to those described in the previous experiment except that 0.1 mole of sodium chloride was added to one of the runs and 0.1 mole of sodium bromide was added to another. The results of these experiments are summarized in Table I.

Reaction of N-Bromotribromoacetamide with Sodium Hydroxide.—A mixture of 15.26 g. (0.041 mole) of N-bromotribromoacetamide (93.5% pure) and 5.85 g. (0.146 mole) of sodium hydroxide in 49 ml. of water was employed in the hydrolysis. An exothermic reaction was observed during the heating at 60°. The volatile product which distilled during the reaction period solidified in the apparatus and was removed by rinsing with ether. The volatile product after isolation was analyzed by gas chromatography using a carbon tetrachloride internal standard. The yields of products obtained are summarized in Table II. Cyanate and cyanide were detected in the residue; oxalate was not.

Hydrolysis of Cyanate during Hofmann Reaction Conditions.—The extent of cyanate hydrolysis under Hofmann conditions was estimated by heating a solution, prepared by dissolving 6.12 g. (0.075 mole) of potassium cyanate and 10.4 g. (0.26 mole) of sodium hydroxide in 120 ml. of water, for 25 min. at 60° and then for 25 min. at 110°. Ninety-three percent of the cyanate was recovered as the dicarbamyl hydrazine.

Hydrolysis of Bromotrichloromethane and Chloroform during Hofmann Reaction Conditions.—A solution consisting of 95.6% bromotrichloromethane and 3.7% of chloroform was added to 120 ml. of water containing 10.4 g. (0.26 mole) of sodium hydroxide and distilled as described in the Hofmann reaction experiments. Analysis of the material in the Barrett trap showed that 91% of the bromotrichloromethane and 60% of the chloroform were recovered.

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