terium oxide had been added, some deuteroalcohol was distilled out of the reaction mixture, b.p. 79.5–80°. After all the deuterium oxide had been added, the crude deuteroalcohol was distilled from the reaction mixture, b.p. 79–83°. The yield was 82.3 g. (88%). The crude deuteroalcohol was then heated at reflux successively: with 38 g. of freshly distilled ethyl orthocarbonate, containing one drop of concentrated sulfuric acid for 12.5 hours; and finally with 75 g. of freshly distilled ethyl orthocarbonate containing one drop of concentrated sulfuric acid for 14.5 hours. After this treatment, the deuteroalcohol was purified by fractional distillation using a ten-inch, helices-packed column, b.p. 77.5–79°, $n^{20}\mathrm{D}$ 1.3635. This main fraction was redistilled using the same column, b.p. 77–78°, $n^{20}\mathrm{D}$ 1.3620, d^{25}_4 0.804. The yield was 49.2 g. (53%). The reported[12] values are b.p. 78.5–79°, $n^{26}\mathrm{D}$ 1.3583,[12] d^{25}_4 0.801.[31]

Isomerization of Allyl *n*-Hexyl Sulfide with Sodium Ethoxide in Deuteroalcohol.—The sulfide (8.0 g., $n^{20}\mathrm{D}$ 1.4688) was refluxed for 14.5 hr. under nitrogen in a solution prepared from 1.4 g. of sodium and 20 ml. of deuteroalcohol ($n^{20}\mathrm{D}$ 1.3620). The solution was worked up as described above, and the product (5.03 g., 63%) was obtained after two distillations; the center cut, which was taken for the mass spectrometric analyses, had the following properties: b.p. 86.7–86.9° (12.5–13 mm.), $n^{20}\mathrm{D}$ 1.4762.

The other runs in deuteroethanol were carried out similarly.

Acknowledgments.—We are greatly indebted to Dr. D. O. Schissler and Dr. D. P. Stevenson of the Shell Development Co. for the mass spectrometric analyses. W. E. L. expresses his appreciation to the American Cyanamid Co. for a Fellowship for the year 1954–1955. We wish to acknowledge helpful discussions with Dr. W. H. Saunders, Jr.

ROCHESTER, N. Y.

[31] T. Chang and Y. Wei, *C. A.*, **42**, 7236 (1948).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE UNIVERSITY]

gem-Dihalides from the Hofmann Degradation of α-Haloamides[1]

BY CALVIN L. STEVENS, TAPAN K. MUKHERJEE[2] AND VINCENT J. TRAYNELIS[3]

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α-Haloamides of acetic, propionic, butyric, isobutyric, methylethylacetic and diethylacetic acids were treated with sodium hypobromite to give *gem*-dihalides. The yields varied from 95% to less than 10%. Cyanate ion formation was found to accompany *gem*-dihalide formation. An α-haloisocyanate was prepared independently and shown not to be an intermediate in the formation of the *gem*-dihalides. Since the corresponding N-bromo-α-chloroamide under Hofmann conditions gave the *gem*-dihalide, but the N-bromoamide in the presence of bromide ion and absence of base did not react, the N-bromoamide ion is indicated as the intermediate which reacts to give the *gem*-halide.

During a previous investigation, which involved the characterization of α-halonitriles, Hofmann degradations of the corresponding amides to ketones were used to show that the halogen atoms were in the α-position.[4] When α-chloro-α-methylbutyramide was subjected to the Hofmann reaction, only a 10% yield of ketone resulted. The identification of the main product from the reaction as a *gem*-dihalide led to the present investigation, which indicates that the reaction has more than limited applicability and, more important, that the conditions of the Hofmann reaction can be varied to increase either the yield of ketone or the yield of *gem*-dihalide.

Kishner,[5] in 1905, attempted the preparation of cyclobutanone *via* a Hofmann degradation of α-bromocyclobutanecarboxamide. The yield of ketone was low, and the other product isolated was considered by Kishner to be 1,1-dibromocyclobutane. To confirm his belief he subjected α-bromoisobutyramide to the same conditions and obtained in 12% yield an oil which contained a small amount of material assumed to be 2-bromopropylene. The main constituent of the oil was the *gem*-dihalide, 2,2-dibromopropane, which was identified by physical constants and by conversion to acetone.

A recent report by Rodionov, Alekseyeva and Vaver[6] on an investigation of the Hofmann degradation with α-bromoaliphatic amides describes the isolation of the corresponding ketones with no mention of *gem*-dihalides. However, Husted and Kohlhase[7] in a study of the Hofmann degradation of aliphatic perfluoroamides report further examples of the formation of *gem*-dihalides (perfluorohalides) and indicate that the reaction proceeds through the N-bromoamide.

In the present study, Kishner's first experiments with α-bromoisobutyramide werer epeated and his results verified. Approximately 10% of 2,2-dibromopropane and 68% of acetone could be isolated from the Hofmann degradation. *Significantly*, a fivefold increase in the yield of *gem*-dihalide was gained by a simple variation of the experimental technique. In the latter experiment, 54% of *gem*-dihalide, 10% of acetone and 31% of α-hydroxyisobutyric acid were isolated. The two procedures differed only in that the first reaction mixture consisting of amide and sodium hypobromite was steam distilled immediately (procedure B) while the latter reaction mixture was allowed to remain at 0–5° for 66 hours (procedure A).

The corresponding α-chloroisobutyramide, when subjected to the latter procedure, gave 95% of 2-chloro-2-bromopropane; procedure B gave only 29% yield of the mixed *gem*-dihalide.

Table I records the yields of *gem*-dihalides obtained from α-haloamides of acetic, propionic, butyric, isobutyric, methylethylacetic and diethylacetic acids. The carbonyl compounds were isolated and identified as 2,4-dinitrophenylhydrazone derivatives. The α-hydroxyacids were isolated by con-

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[2] Supported in part by a Grant-in-aid from the Research Corporation of New York.

[3] Ethyl Corporation Predoctoral Fellow.

[4] C. L. Stevens and T. H. Coffield, THIS JOURNAL, **73**, 103 (1951).

[5] N. Kishner, *J. Russ. Phys. Chem. Soc.*, **37**, 103, 106 (1905); *Chem. Centr.*, **76**, I, 1219, 1220 (1905).

[6] V. M. Rodionov, E. N. Alekseyeva and V. A. Vaver, *Zhur. Obschei Khim.*, **23**, 1842 (1953).

[7] D. R. Husted and W. L. Kohlhase, THIS JOURNAL, **76**, 5141 (1954).

TABLE I

HOFMANN REACTIONS WITH α-HALOAMIDES

Amide, m.p.,C° .	Method	Carbonyl compound, yield, %	*gem*-Dihalide	Crude yield, %	Acid	Yield %
α-Chloroacetamide, 118–120	B	Formaldehyde	$ClCH_2Br$	7	$HOCH_2COOH$	9
α-Chloropropionamide,[a] 75–77	A		$CH_3CHClBr$	13		
α-Chloropropionamide,[a] 75–77	B	Acetaldehyde, 1	$CH_3CHClBr$	64	$CH_3CHOHCOOH$	22
α-Bromopropionamide,[b] 122–123	A		CH_3CHBr_2	8		
α-Bromopropionamide,[b] 122–123	B	Acetaldehyde, 1	CH_3CHBr_2	41	$CH_3CHOHCOOH$	20
α-Chlorobutyramide,[c] 75–77	B	Propionaldehyde, 1	$CH_3CH_2CHBrCl$	46	$C_2H_5CHOHCOOH$	24
α-Bromobutyramide,[b] 109–110	B	Propionaldehyde, 1	$CH_3CH_2CHBr_2$	20	$C_2H_5CHOHCOOH$	50
α-Chloroisobutyramide,[d] 118–120	A	Acetone, 1	$CH_3CBrClCH_3$	95	$(CH_3)_2CHOHCOOH$	1
α-Chloroisobutyramide,[d] 118–120	B	Acetone, 1	$CH_3CBrClCH_3$	29		
α-Bromoisobutyramide,[d] 148–149	A	Acetone, 10	$CH_3CBr_2CH_3$	54	$(CH_3)_2CHOHCOOH$	31
α-Bromoisobutyramide,[d] 148–149	B	Acetone, 68	$CH_3CBr_2CH_3$	9		
α-Chloromethylethylacetamide,[e] 36–37	B	Methyl ethyl ketone, 3	$C_2H_5CClBrCH_3$	56	$C_2H_6(CH_3)CHOHCOOH$	36
α-Chlorodiethylacetamide,[e] 56–58	B	Diethyl ketone, 4	$C_2H_5CClBrC_2H_5$	73	$(C_2H_5)_2CHOHCOOH$	17

[a] H. Backunts and R. Otto, *Ber.*, **9**, 1592 (1876). [b] C. A. Bischoff, *ibid.*, **30**, 2312 (1897). [c] O. DeBoosere, *Bull. soc. chim. Belg.*, **32**, 44 (1923). [d] C. L. Stevens, THIS JOURNAL, **70**, 166 (1948). [e] C. L. Stevens and T. H. Coffield, *ibid.*, **73**, 103 (1951).

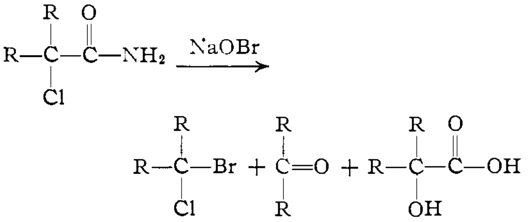
TABLE II

gem-DIHALIDES

Halide	B.p., °C.	$n^{20}D$	d^{20}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_2BrCl[a]	66–67[a]	1.4832[b]	1.938[a]	9.28	8.97	1.55	1.76
$CH_3CHBrCl$	82–83[c]	1.4662[c]	1.667[d]	16.75	17.13	2.81	2.99
CH_3CHBr_2	108–109[e]	1.5125[f]	2.104[e]	12.78	13.14	2.15	2.25
$CH_3CH_2CHBrCl$	110–111[g]	1.4686[g]	1.536[h]	22.88	22.88	3.84	3.95
$CH_3CH_2CHBr_2$	134–135[g]	1.5084[g]	1.921	17.84	18.06	3.00	3.26
$CH_3CBrClCH_3$[g]	90.5–91.5[g]	1.4572[g]	1.495[h]	22.88	22.98	3.84	3.89
$CH_3CBr_2CH_3$[g]	112–113[g]	1.4983[g]	1.880[i]	17.84	17.90	3.00	3.17
$C_2H_5CBrClCH_3$[j]	119–120	1.4640	1.408	28.01	28.32	4.70	5.02
$C_2H_5CBrClC_2H_5$[j]	145–147	1.4108	1.373	32.37	32.48	5.43	5.56

[a] L. Henry, *J. prakt. Chem.*, [2] **32**, 431 (1885). [b] J. R. Lachner, R. E. Scruby and J. D. Park, THIS JOURNAL, **72**, 523 (1950). [c] M. S. Kharasch and C. W. Hannum, *ibid.*, **56**, 712 (1934). [d] W. Stadel and J. Denzel, *Ann.*, **195**, 193 (1879). [e] W. H. Perkin, *J. Chem. Soc.*, **45**, 519 (1884). [f] R. Weegmann, *Z. physik. Chem.*, **2**, 257 (1888). [g] M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2**, 300 (1937). [h] J. Reboul, *Ann. chim. phys.*, [5] **14**, 482 (1878). [i] N. Kishner, *J. Russ. Phys. Chem. Soc.*, **37**, 103 (1905). [j] *n* and *d* at 23°.

tinuous ether extraction and identified by preparation of crystalline derivatives.



$$R-\overset{\displaystyle R}{\underset{\displaystyle Cl}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{NaOBr} R-\overset{\displaystyle R}{\underset{\displaystyle Cl}{C}}-Br + \underset{\displaystyle R}{\overset{\displaystyle R}{C}}=O + R-\overset{\displaystyle R}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH \quad (1)$$

The physical constants for the *gem*-dihalides are listed in Table II, and were used for identification by comparison with values recorded in the literature. The analyses and molar refractivities of the compounds corresponded to those for the proposed empirical formulas. Finally, four *gem*-dihalides, obtained independently, were shown to be identical with the products of the Hofmann degradation by comparison of their infrared spectra and physical properties.

A reasonable material balance was obtained for many of the reactions. However, when the carbonyl compounds produced were aldehydes, they never could be isolated from the strong basic solution in greater than 1% yield and the material balance consequently suffered.

Examination of Table I will reveal that invariably the chloroamide gave a better yield than did the corresponding bromoamide. Further, procedure A was not always the preferred procedure, since with α-chloropropionamide procedure B gave 64% of *gem*-dihalide while procedure A gave only a 13% yield.

Initial experiments in the investigation of the mechanism of the reaction were designed to show in what form the carbonyl carbon and amide nitrogen of the original α-haloamide appeared in the final reaction mixture. The presence of cyanide ion could be demonstrated in some of the reaction mixtures by conversion to Prussian Blue, but the lack of correspondence between the yield of *gem*-dihalide and cyanide ion indicated that the cyanide ion was not produced in the Hofmann reaction but rather by the action of strong base upon the α-haloamide.[8]

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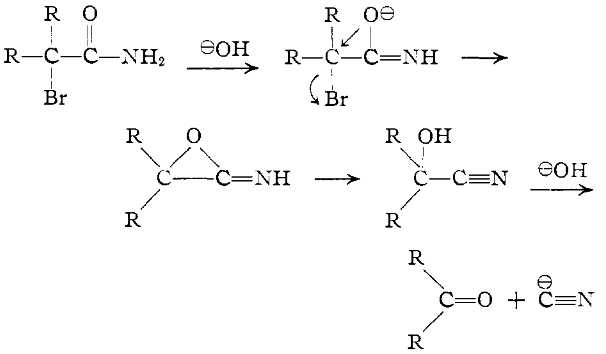
(8) G. Mossler (*Monatsh.*, **29**, 69 (1908)) reported that the action of 20% potassium hydroxide on α-bromoamides gave rise to the same carbonyl compounds produced by the Hofmann reaction, together with cyanide ion. The resulting ketones were identified but the yield of the reaction was determined only by measuring the amount of cyanide ion. The reasonable assumption was made that the cyanide ion and ketone were derived from the same α-haloamide molecule. One route for the formation of the products in this interesting but little studied reaction might be through the cyanohydrin.

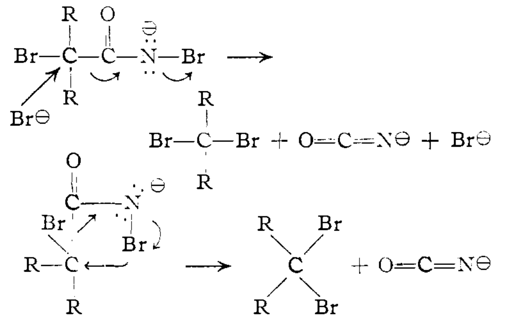


In the formation of *gem*-dihalides, the carbon-nitrogen fragment of the original haloamide was shown to be cyanate ion by the preparation of the hydrazodicarboxamide derivatives[9] in yields corresponding to the yields of *gem*-dihalides.

The formation of cyanate ion in the Hofmann reaction is not unknown; Arcus, *et al.*, reported that the reaction of an α-hydroxyamide[10] or an α-ketoamide[11] under Hofmann conditions gave cyanate ion.

Next, an attempt was made to find the point at which the reaction which produced the *gem*-dihalide diverged from the ordinary Hofmann reaction. An N-bromo-α-chloroamide was prepared independently and subjected to the conditions of the Hofmann reaction; *gem*-dihalide was produced. However, the corresponding α-haloisocyanate was hydrolyzed immediately by water containing bromide ion to give only the ketone, indicating that the N-bromoamide is an intermediate but that the α-haloisocyanate is not. This latter conclusion was also reached by Husted and Kohlhase.[7]

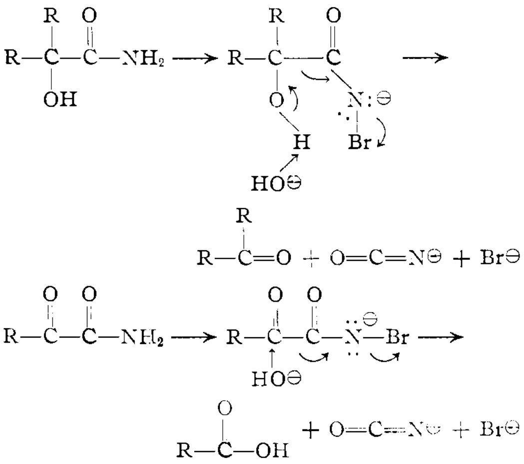
Since the N-bromoamide in the presence of bromide ion and absence of base did not give *gem*-dihalide, one reasonable conclusion is that the N-bromoamide ion is the intermediate that reacts to give *gem*-dihalide and cyanate ion. Whether the reaction involves displacement by bromide ion, as indicated in equation 2, or a cyclic mechanism, as indicated in equation 3, is now under investigation.



(2)

(3)

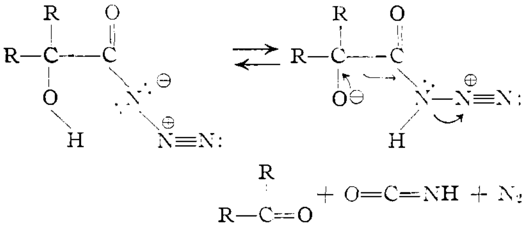
These experiments suggest the following alternate mechanisms to the ones proposed by Arcus, *et al.*, for the Hofmann reaction of α-hydroxyamides[10] and α-ketoamides.[11]



(4)

(5)

Further, the decomposition of α-hydroxyacyl azides, which produces carbonyl compounds and cyanic acid, probably proceeds without prior rearrangement to the isocyanate.[12]



(6)

The Hofmann reaction reported in this paper accomplishes the same result as the decomposition of the silver salts of α-haloacids with elemental halogen. The present reaction conditions appear to be much less rigorous, and in certain cases this appears to be the method of choice.

Experimental

α-Haloamides.—The starting α-haloamides were prepared according to the methods available in the literature and were recrystallized until they had constant melting points. The melting points, which agree with those previously recorded, are listed in Table I along with the appropriate references.[13]

Preparation of *gem*-Dihalides.—Table I lists the starting amides, the yields of the *gem*-dihalides, and the yields of the carbonyl components and hydroxyacids in those cases where a material balance was determined. An example of the detailed experimental conditions is presented for both procedures A and B.

Procedure A with α-Bromoisobutyramide.—A solution of sodium hypobromite was prepared by the addition of 19.2 g. (0.12 mole) of bromine to a solution of 14.4 g. (0.36 mole) of sodium hydroxide in 120 ml. of water at 0°. After 14.0 g. (0.084 mole) of powdered α-bromoisobutyramide was dissolved, the solution was stirred an additional ten minutes and then cooled to 0–5° for 66 hours. At the end of this period, the mixture was heated to 50° and shaken until the white solid dissolved. The oil was removed and amounted to 9.1 g. (54% crude yield) of 2,2-dibromopropane. The reaction medium was distilled until 5 ml. of cloudy distillate was collected. Acetone was present in the distillate in 10% yield and was isolated and identified as the 2,4-dinitrophenylhydrazone. The residue from the distillation contained

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[9] R. A. Weerman, *Rec. trav. chim.*, **37**, 16 (1917).

[10] C. L. Arcus and D. B. Greenwood, *J. Chem. Soc.*, 1937 (1953).

[11] C. L. Arcus and B. S Prydal, *ibid.*, 4018 (1954).

[12] *Cf.* the chapter describing the Curtius reaction in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. 3, 1946, pp. 350-351.

[13] Detailed directions for the preparation of the amides are available in the Ph.D. thesis of Vincent J. Traynelis, Wayne University, 1953.

cyanide ion as shown by conversion to Prussian Blue. The residue was acidified with dilute sulfuric acid and extracted continuously with ether for 40 hours. The ether was removed and the acid residue dissolved in distilled water. This solution gave a negative test with silver nitrate, indicating the absence of hydrobromic acid in the ether extract. Titration of the above solution showed the presence of 31% acid, which was identified as α-hydroxyisobutyric, m.p. 80°, by mixture melting point with an authentic sample and by the preparation of its *p*-nitrobenzyl ester, m.p. 79–80°.

After drying the 2,2-dibromopropane over calcium chloride, distillation from a 10-ml. distilling flask gave 6.7 g. (39%) of *gem*-dihalide, b.p. 111–116°. An analytical sample was obtained by fractionation through a 30 × 0.8 cm. column at atmospheric pressure, b.p. 112–113°, n^{23}D 1.4971, d^{20}_4 1.880. The infrared spectra of the analytical sample, the once-distilled material, and the crude *gem*-dihalide were essentially identical.

Procedure B with α-Chloropropionamide.—A solution of 16.0 g. (0.40 mole) of sodium hydroxide in 140 ml. of water was treated with 19.2 g. (0.12 mole) of bromine to give the sodium hypobromite solution used. After 10 g. (0.10 mole) of powdered α-chloropropionamide was dissolved and stirred ten minutes, the solution was heated rapidly and 15 ml. of distillate collected. The oil separated from the distillate and amounted to 9.2 g. (64% crude yield) of 1-bromo-1-chloroethane. From the aqueous portion of the distillate was isolated 1% of acetaldehyde as the 2,4-dinitrophenylhydrazone, m.p. 147–148°. The residue after distillation was acidified with dilute sulfuric acid and extracted with ether continuously for 20 hours. The ether was removed and the residue dissolved in water. Titration showed the presence of 22% acid, which was identified as lactic acid by the phenacyl ester derivative, m.p. 94–95°.

Purification by distillation, after drying over calcium chloride, gave 7.7 g. (53%) of 1-bromo-1-chloroethane. The analytical sample obtained as previously described had the following physical constants: b.p. 82–83°, n^{20}D 1.4662, d^{20}_4 1.667.

The physical properties and analyses of the *gem*-dihalides are given in Table II.

Independent Synthesis of *gem*-Dihalide.—2,2-Dibromopropane (30% from 2-bromopropene), 2-bromo-2-chloropropane (12% from 2-chloropropene) and bromochloromethane (31% from chloroiodomethane) were prepared independently by methods available in the literature. References to these methods are included in Table II. 1,1-Dibromoethane was available from Eastman Kodak Co. and was purified by distillation from comparison purposes. The physical properties and infrared spectra of the *gem*-dihalides prepared independently were identical with those obtained from the Hofmann degradation.

Preparation of N-Bromo-α-chloroisobutyramide.—To a stirred solution of sodium hypobromite, made by dissolving 16 g. (0.1 mole) of bromine in 50 ml. of water containing 12 g. (0.3 mole) of sodium hydroxide, 12.15 g. (0.1 mole) of powdered α-chloroisobutyramide was added at −5°. When all the amide was dissolved and the solution became colorless the temperature was allowed to rise to 2°. The solution was filtered through a sintered glass funnel into a cold solution of 25 ml. of glacial acetic acid in 25 ml. of water. The clear filtrate was cooled to −10°, at which temperature the N-bromoamide precipitated. The N-bromoamide was filtered and dried on a porous plate. The crude yield was 11.6 g. (60.5%), m.p. 63–66° dec. Recrystallization from chloroform gave colorless needles, m.p. 68–70° dec.

Anal. Calcd. for $C_4H_7BrClNO$: Br, 39.89. Found: Br, 39.80.

The active bromine was determined by dissolving the N-bromoamide in glacial acetic acid, adding an aqueous solution of potassium iodide, and titrating with standard sodium thiosulfate solution.

Reaction of N-Bromo-α-chloroisobutyramide with Sodium Hydroxide and Sodium Bromide (Hofmann Conditions).—To a solution of 0.08 g. (0.002 mole) of sodium hydroxide and 0.2 g. (0.002 mole) of sodium bromide in 15 ml. of water was added 2 g. (0.001 mole) of N-bromo-α-chloroisobutyramide at 0°. The N-bromo-α-chloroisobutyramide dissolved rapidly and the temperature was allowed to rise slowly to 25°. After 4 hours an oil had separated, 0.135 g. (86%). After the oil was dried over concentrated sulfuric acid the weight was 0.125 g. (78%), b.p. 91–92°, n^{20}D 1.4570. The infrared spectrum was identical with that of 2-bromo-2-chloropropane, prepared independently.

Next, 1 g. of N-bromoamide (0.5 millimole) was dissolved in 50 ml. of water. On addition of 0.1 g. (1 millimole) of sodium bromide at 0°, bromine was liberated slowly. After 12 hours at 0°, no oil separated.

To 25 ml. of the above solution, excess sodium acetate was added, followed by a saturated solution of semicarbazide hydrochloride. The fact that no solid separated indicated the absence of cyanate ion.

The amount of active bromine left in the solution was determined by titrating a 25-ml. aliquot of the original reaction mixture, using the sodium thiosulfate procedure. The results indicated that the reaction mixture contained 95% active bromine in the form of N-bromoamide, hypobromous acid or bromine, as indicated by the equilibria

$$\mathrm{Br}^{\ominus} + \mathrm{RCONHBr} + \mathrm{H_2O} \leftrightarrows \mathrm{RCONH_2} + \mathrm{HOBr} + \mathrm{Br}^{\ominus} \leftrightarrows \mathrm{RCONH_2} + \mathrm{Br_2} + {}^{\ominus}\mathrm{OH}$$

Hydrolysis of 2-Chloro-2-propyl Isocyanate.—Into a system protected by calcium chloride drying tubes was placed 75 ml. of anhydrous *n*-amyl ether and 7.15 g. (0.11 mole) of freshly activated[14] sodium azide. The suspension was stirred and cooled to 0° and 14.1 g. (0.1 mole) of α-chloroisobutyryl chloride added over a period of one hour. The mixture was then heated slowly to 70°, at which temperature a vigorous reaction took place, accompanied by the evolution of nitrogen, 2.5 l. of which was collected. The mixture was heated to 80–85° for an additional 25 minutes and the isocyanate distilled directly from the reaction mixture, b.p. 26–28° (110 mm.), 3.8 g. (31%). The isocyanate was a strong lachrymator which polymerized quickly at room temperature. In another experiment, material which boiled at 53–56° in a nitrogen atmosphere had n^{25}D 1.4480 and had a strong band at 4.4 μ in the infrared spectrum. The freshly distilled isocyanate (0.97 g.) was added to 10 ml. of water containing 1.6 g. of sodium bromide and cooled to 0°. An immediate evolution of carbon dioxide occurred and after 24 hours an aliquot was added to 2,4-dinitrophenylhydrazine reagent. Acetone dinitrophenylhydrazone was isolated in an amount corresponding to 74% yield from the isocyanate and identified by mixture melting point with a known sample. There was no evidence of *gem*-dihalide formation.

In a further experiment, 1.02 g. of the freshly distilled colorless isocyanate was added to 25 ml. of water at room temperature. After the evolution of carbon dioxide, an aliquot was used for the determination of ionic chlorine. The fact that 90% of the theoretical amount of chloride ion was present in the aqueous solution indicated that the original isocyanate contained not more than 10% α,β-unsaturated isocyanate[15] as impurity. Acetone dinitrophenylhydrazone could be isolated in 97% yield from another aliquot.

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(14) *Cf.* ref. 12, page 382.

(15) H. D. Zook, M. Ream and E. W. Delchamps (THIS JOURNAL, **75**, 5590 (1953)) report the Curtius rearrangement of α-bromodineopentylacetyl azide to give the α,β-olefinic isocyanate as the first isolable product.