[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF COLORADO]

The Preparation and Brominating Properties of Some Halogenated N-Bromoacetamides[1]

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The syntheses of the N-bromo derivatives of monochloro-, dichloro-, trichloro, difluoro- and trifluoroacetamide are described. The various N-bromoacetamides (abbreviated NBA) reacted at reflux temperature with an excess of toluene to give benzyl bromide as the exclusive monobrominated product. It was observed that halogen substituents on the α-carbon atom of NBA gradually increased the nuclear bromination of toluene (at room temperature) in the following order: $-CH_3 < -CCl_3 < -CCl_2H < -CClH_2 < -CF_3$. The product of the nuclear bromination of toluene was predominantly *p*-bromotoluene. The ability of the halogenated N-bromoacetamides to produce "allylic" bromination of cyclohexene decreased in the following order: $-CH_3 > -CCl_2H > -CCl_3 > CClH_2 > CF_3$. N-Bromotrifluoro- and N-bromotrichloroacetamide formed considerable amounts of addition products with cyclohexene. Benzaldehyde was obtained in 64–70% yield by the interaction of benzyl alcohol with NBA, trichloro NBA and dichloro NBA. The brominating properties of these halogenated N-bromoacetamides strongly suggest useful adaptations in a variety of synthetic reactions.

The side-chain bromination of toluene at room temperature by N-bromosuccinimide may be accomplished readily by adding dibenzoyl peroxide to the reaction mixture.[2] When equimolar amounts of certain metal chlorides (Lewis acids) are added, nuclear bromination of toluene readily can be achieved.[3] Henne[4] has shown that N-bromosuccinimide (abbreviated as NBS) brominates toluene exclusively in the side chain at 90°; whereas under the same conditions perfluorinated N-bromosuccinimide favored nuclear bromination of toluene. Thus, it appears that perfluorination of the imide ring accentuates the electronegative effect of the imide ring which in turn enhances the positive character of the N-bromine sufficiently to cause ionic or nuclear bromination of toluene without the aid of Lewis acid catalysts.

The purpose of this study was to prepare N-bromo substituted acetamides having varying numbers of halogens present on the α-carbon atom, and to determine the brominating properties of these compounds. It will be shown that under the conditions studied such halogen substituents produced significant ionic brominating properties as demonstrated by the reactions of each compound with toluene and cyclohexene.

The syntheses of the N-bromoacetamides listed in Table I are given in the experimental section.

TABLE I

HALOGENATED N-BROMOACETAMIDES

Compound	M.p.,[a] °C.	Yield, %	Bromine analyses, % Found	Theory
$ClH_2CCONHBr$	75	61.0	46.37	46.37
$Cl_2HCCONHBr$	96	76.0	38.57	38.64
$Cl_3CCONHBr$	125	81.0	33.01	33.10
$CF_3CONHBr$	62	63.0	41.70	41.67
$CF_3HCONHBr$	43	40.0	46.01	45.99

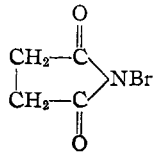
[a] All melting points were determined on a Fisher–Johns melting point block and are uncorrected. Analyses were determined by KI–$Na_2S_2O_3$ titrations.

Lengfeld and Stieglitz[5] prepared N-bromosuccinimide by allowing the imide to react with bromine in aqueous, alkaline medium. This method gave little or none of the desired halogenated N-bromoacetamides. Borsmenu's procedure[6] for the preparation of the N-bromoformamide, employing bromine and silver oxide in ethyl acetate, was also adapted to the synthesis of N-bromo-α-chloroacetamide. Competitive bromination of the solvent, however, complicated considerably the isolation of the desired products. Francescini[7] prepared crude N-bromomonochloroacetamide by treating the mercury salt of the corresponding amide with bromine in chloroform. The final product, however, contained appreciable amounts of 1-bromo-1-chloroacetamide which could not be removed. These methods were abandoned in favor of the mild bromination of the corresponding halogenated amide in anhydrous trifluoroacetic acid[4] to give pure N-bromo compounds in relatively high yields.

At room temperature the reaction of several bromoamides with toluene resulted in the products indicated in Table II.

TABLE II

BROMINATION OF TOLUENE

Compound	Amide recovery, %	Conversion to C_7H_7Br, %	Ratio of C_7H_7Br Br-C_6H_5-CH_3	C_6H_5-CH_2Br
$CH_3CONHBr$	86.0	50.0	0.0	100.0
$CCl_3CONHBr$	92.0	58.0	17.0	83.0
$CCl_2HCONHBr$	90.0	64.0	62.0	38.0
$CClH_2CONHBr$	98.0	70.0	82.0	18.0
$CF_3CONHBr$	91.0	68.0	88.0	12.0
	91.0	68.0	0.0	100.0

A series of color changes slowly accompanies all the bromination reactions of toluene at room temperature. The solution changed from yellow to orange, to deep red, and finally back to yellow. At this point the reaction mixture was tested with potassium iodide solution; when no liberation of iodine was noted, the reaction was considered completed. No bromination of toluene occurred, however, when N-bromoacetamide and N-bromosuccinimide were stirred in excess toluene at room temperature for 24 hours. Slight heating was necessary to bring about completeness of reaction.

(1) Abstracted from the thesis of H. J. Gerjovich presented in partial fulfillment for the degree of Doctor of Philosophy, June, 1951. This work was supported in part by the Office of Naval Research.

(2) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(3) H. Schmid, *ibid.*, **29**, 1144 (1946).

(4) A. L. Henne and W. F. Zimmer, THIS JOURNAL, **73**, 1103 (1951).

(5) F. Lengeld and J. Stieglitz, *Am. Chem. J.*, **15**, 215 (1893).

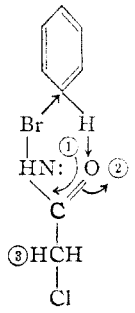
(6) R. Borsmenu, *Compt. rend.*, **153**, 949 (1911).

(7) G. Francescini, *Gazz. chim. ital.*, **33**, 228 (1903).

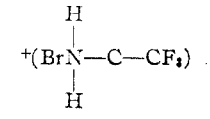
Possible Mechanisms.—If we consider, for the sake of discussion, that N-bromoacetamide is the standard compound in Table II, and that under the reaction conditions a homolytic cleavage ($RCONH\cdot + Br\cdot$) is normal; then the increasing nuclear or ionic bromination of toluene may be attributed to the increasing positive character of the N-bromine in the halogenated acetamides. An attempt to correlate the ionic bromination of toluene with increasing -I effect (induction) due to the gradual increase of halogen substituents on the alpha carbon atom of the N-bromoacetamides resulted in contradiction with the experimental data. It may be observed that ionic bromination of toluene by R–CO–NHBr increased with changes in R as: $R = CH_3 < CCl_3 < CCl_2H < CClH_2 < CF_3$ rather than the expected order: $CH_3 < CClH_2 < CCl_2H < CCl_3 < CF_3$.

It is highly questionable that bromination of toluene to give both benzyl bromide and monobromotoluene should occur by the same mechanism. Djerassi[8] stated that it was likely that N-bromosuccinimide might react by several mechanisms resulting from homolytic as well as heterolytic dissociation of the reagent. In this present work then, it would appear that a homolytic dissociation (free radical bromination) of the reagents gave benzyl bromide, whereas a heterolytic cleavage (ionic bromination) gave monobromotoluene. A heterolytic cleavage of the N-bromo compounds in anhydrous toluene, would require much greater energy (coulombic effect) than a homolytic cleavage. Thus, it is highly probable that ionic bromination of toluene proceeded *via* complex formations which aid the ionic cleavage of the halogenated N-bromo compounds. Two such complexes are proposed as

I



II



Two competing factors must be considered which may limit the formation and stability of the suggested push-pull, six-membered ring complex (structure I above). As the inductive effect (3) increases (with increasing halogen substituents on the α-carbon), electron shift (1) is favored, however, shift (2) (basicity of the oxygen) is hindered. It is assumed both shifts of electrons are equally important, and that the relative loss of either effect will decrease the probability of complex formation and ionic bromination of toluene. Thus the order $CH_3 < CCl_3 < CCl_2H < CClH_2$ previously postulated as denoting increasing positive character of the N-bromine is instead (in accordance with complex structure (I)) an order of decreasing basicity of the oxygen atom: $CH_3 > CCl_3 > CCl_2H > CClH_2$. It is to be noted that N-bromoacetamide gave benzyl bromide exclusively even though the carbonyl oxygen in this reagent is theoretically most basic. The bromine in this case is not sufficiently positive to undergo such complex formation as structure I. The consideration of the two competing factors described previously for the complex formation seems to explain the reactions of N-bromoacetamide and N-bromo- (mono-, di-, tri-) chloroacetamides with toluene. This argument, however, fails to explain the predominantly ionic reaction of N-bromotrifluoroacetamide with toluene. Since perfluorinated N-bromoacetamide dissolved readily in toluene with a negative heat of solution and then under certain conditions reacted with toluene in a matter of minutes with sufficient exothermic heat to bring the solution to a boil (the chlorinated N-bromo compounds did not behave in this manner) its ionic behavior we believe is better explained by the formation of complex II $(BrNH_2C(=O)—CF_3)^+$.

Buckles[9] has shown that N-bromoacetamide was capable of brominating the double bond of styrene in 30–50% yields; however, if anhydrous HBr was added to the reaction dibromostyrene conversion was increased to 95% with the reaction complete in a matter of minutes. The following scheme was presented to explain his results

$$AcNHBr + HBr \longleftrightarrow AcNH_2Br^+ + Br^-$$
$$AcNH_2Br^+ + Br^- \longleftrightarrow AcNH_2 + Br_2$$

Similarly Derbyshire and Waters[10] have suggested that the addition of sulfuric acid to N-bromosuccinimide reaction on toluene made possible a more powerful brominating agent, namely: $R_2N\text{-}Br + H^+ \leftrightarrow (R_2NH\text{-}Br)^+ \leftrightarrow R_2NH + Br^+$ and that aromatic substitution by such reagents proceed *via* their conjugate acids. In this present work HBr may be formed by the action of a bromine-free radical on toluene. The HBr thus formed then could react with the N-bromo compound to give the complex $^+(BrH_2NCOR)$. In accordance then with the proposed complex structure II (conjugate acids of the N-bromo compounds) the increasing order of ionic bromination of toluene (see Table II) as $R—C(=O)—NHBr$ (where $R = CH_3 < CCl_3 < CCl_2H < CClH_2 < CF_3$) represents or depends upon the ease of formation and stability of the corresponding conjugate acids, $(BrNC(=O)—R)^+$. There are other factors to consider before such mechanisms can be accepted. The activation energy requirements for each N-bromo-compound, reaction rates, and inter-hydrogen bonding[11] of N-bromo compounds should be studied. Also, the various structural features of the N-bromoamides may have profound effects on the free-radical, side-chain brominations. These effects would cause wide deviations in predicted results.

(8) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

(9) R. E. Buckles, THIS JOURNAL, **71**, 1157 (1949).

(10) C. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573 (1950).

(11) R. E. Richards and N. W. Thompson, *ibid.*, 2348 (1947).

When cyclohexene and the N-bromo compounds were allowed to react at room temperature, the products shown in Table III were obtained.

TABLE III

BROMINATION OF CYCLOHEXENE

Compound	3-Bromocyclohexene, %	Dibromocyclohexane, %	Adduct, %	Recovery amide, %
$CH_2ClCONHBr$	13.0	16.0	Decomposed	53.0
$CCl_2HCONHBr$	50.0	15.0	..	80.0
$CCl_3CONHBr$	19.0	Trace	60.0	..
$CF_3CONHBr$	..	32.0	38.0	20.0
$CH_3CONHBr$	62.0	13.0	..	85.0

In all cases, 0.1 mole of N-bromo compound was combined with 1.0 mole of freshly distilled cyclohexene at room temperature. After a short induction period, the mixture became warm and, in a matter of minutes, exothermic enough to bring the cyclohexene to a boil. External cooling was required to prevent excessive boiling. After a few minutes, the exothermic reaction ceased, and the reaction cooled down to room temperature. The reaction was considered complete when no liberation of iodine was observed by shaking a portion of the cyclohexene mixtures with potassium iodide solution.

It may be observed (Table III) that the halogenated N-bromo compounds are inferior to N-bromoacetamide as "allylic" brominating agents. The "allylic" bromination of cyclohexene to yield 3-bromocyclohexene, has been explained by a free radical mechanism.[12] Thus, if we arrange the N-bromo compounds in Table III in an order of decreasing yields of 3-bromocyclohexene isolated, the increasing positive character of the N-bromine may be arranged as follows: $CH_3CONHBr$ > $Cl_2HCCONHBr$ > $Cl_3CCONHBr$ > $ClH_2CCONHBr$ > $F_3CCONHBr$. Since the bromination of toluene to benzyl bromide and the bromination of cyclohexene to 3-bromocyclohexene have both been postulated as proceeding by a free radical mechanism, the following order arranged in decreasing amounts of benzyl bromide formed (see Table II), should also represent, the order of increasing positive character of the N-bromine in the halogenated acetamides: $CH_3CONHBr$ > $Cl_3CCONHBr$ > $Cl_2HCCONHBr$ > $ClH_2CCONHBr$ > $F_3CCONHBr$. It is to be noted that the above arbitrary arrangements compare quite well, except for the reversal of the di- and trichloro N-bromo compounds in the two arrangements.

During the course of this investigation, it was determined that aqueous silver nitrate would not react with the N-bromo compounds studied. Alcoholic silver nitrate, however, caused a precipitate of silver bromide, indicating the oxidizing power of the N-bromine. Hebbelynck and Martin[13] have reported recently that N-chlorosuccinimide oxidized benzyl alcohol to give good yields of benzaldehyde. Reich and Reichstein[14] have reported that NBA oxidizes secondary alcohols to ketones. Fieser and Rajagopalan[15] have also investigated this reaction with both NBA and NBS. One interesting reaction is the oxidation of cholic acid with NBA to the 7-keto derivative. It was believed that N-bromo compounds could similarly make this conversion directly in anhydrous medium. Benzaldehyde in yields of 64–70% was obtained by allowing benzyl alcohol to react at room temperature with N-bromoacetamide and the di- and trichloro analogs. A more critical study of the possible synthetic applications of oxidation by N-bromoacetamide derivatives is in progress.

(12) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(13) Hebbelynck and R. H. Martin, *Experientia*, **5**, 69 (1949).

(14) Reich and Reichstein, *Helv. Chim. Acta*, **26**, 562 (1943).

(15) Fieser and Rajagopalan, THIS JOURNAL, **71**, 3935 (1949); **72**, 5530 (1950).

Experimental Part

N-Bromotrichloroacetamide.—Trichloroacetic acid (163 g. or 1 mole) was esterified with commercial absolute ethanol (128 g. or 3.0 moles), by boiling the mixture under reflux in a conventional azeotropic distillation apparatus for the removal of water. The ethyl ester, obtained in 96% yield, was shaken with excess ammonium hydroxide as described by Morrell.[16] The trichloroacetamide was obtained by filtering the white precipitate formed, washing with benzene, and crystallizing from hot benzene.

To a solution of 23 g. of silver oxide (0.1 mole) in 250 ml. of anhydrous CF_3COOH (Minnesota Mining and Mfg. Co.) was added 32 g. (0.2 mole) of trichloroacetamide. The reaction mixture was stirred at room temperature for 1 hour, after which a solution of 32 g. of bromine (0.2 mole) in 150 ml. of trifluoroacetic acid was added dropwise, with stirring, from a dropping funnel. After all of the bromine had been added, stirring was continued for an additional half-hour. The silver bromide which formed was filtered on a sintered-glass disc and washed well with fresh trifluoroacetic acid. The filtrate was distilled at room temperature under 20 mm. pressure. As the solvent was removed a solid separated gradually from the solution. When approximately three-quarters of the solvent (CF_3COOH) had been removed, distillation was stopped. The solid which had separated was removed by filtration and washed twice with fresh, cold trifluoroacetic acid, then evacuated for one hour at room temperature under 10 mm. pressure. The solid (29.0 g. or 60% yield) thus obtained was shown to be N-bromotrichloroacetamide, m.p. 124–125°. Additional product was obtained by further removal of solvent from the mother liquor. The residue was recrystallized from carbon tetrachloride yielding 10 g. of N-bromotrichloroacetamide, m.p. 125°. An over-all conversion to N-bromotrichloroacetamide of 81% was thus obtained. Some loss of compound may be attributed to entrainment or sublimation of the N-bromo compound during the removal of solvent.

Anal. Calcd. for C_2HBrCl_3NO: Br, 33.12. Found: Br, 32.98.

N-Bromodichloroacetamide.—Ethyl dichloroacetate and dichloroacetamide were prepared by a procedure similar to that described above. The amides were treated with silver oxide and bromine in trifluoroacetic acid as described for the preparation of N-bromotrichloroacetamide. An over-all yield of 76% of N-bromodichloroacetamide was obtained, m.p. 96°.

Anal. Calcd. for $C_2H_2BrCl_2NO$: Br, 38.64. Found: Br, 38.57.

N-Bromomonochloroacetamide.—Ethyl chloroacetate was converted to the corresponding amide by adapting the classical anhydrous ammonia and ether procedure described by Gilman and Jones.[17] Chloroacetamide was treated in trifluoroacetic acid with silver oxide and bromine as previously described for N-bromotrichloroacetamide. The N-bromo compound did not separate out during the removal of the solvent; practically complete removal of solvent followed by chilling was necessary before crystallization of the semi-liquid residue occurred. The crude residue was purified by crystallization from carbon tetrachloride or by sublimation. N-Bromomonochloroacetamide was obtained in 61% yield as white needles, m.p. 75°.

Anal. Calcd. for $C_2H_3BrClNO$: Br, 46.37. Found: Br, 46.34.

(16) J. Morrell, *J. Chem. Soc.*, **105**, 2705 (1914).

(17) H. Gilman and R. G. Jones, THIS JOURNAL, **65**, 1458 (1943).

N-Bromotrifluoroacetamide.—The method described by Gilman and Jones[17] was used to prepare ethyl trifluoroacetate and the corresponding amide. After treating the amide with silver oxide and bromine in trifluoroacetic acid, filtering off the silver bromide and distilling the filtrate under reduced pressure, a semi-solid residue was obtained. Pure N-bromotrifluoroacetamide (m.p. 63°) was obtained in 63% yield by subliming this crude residue at 60° under 5 mm. pressure.

Anal. Calcd. for C_2HBrF_3NO: Br, 41.67. Found: Br, 41.70.

N-Bromodifluoroacetamide.—The method described by Gilman and Jones[17] was adapted to prepare ethyl difluoroacetate. Apparently, this ester and ethyl alcohol form a constant boiling mixture at 72° at 628 mm. Two layers were formed when 100 ml. of water was added to this distillate. The bottom layer was separated, dried over calcium chloride and finally distilled over P_2O_5. An 80% yield of ethyl difluoroacetate, b.p. 92° at 628 mm., was obtained. The interaction of this ester with anhydrous ammonia gave the corresponding amide which was purified by sublimation, m.p. 51°. The amide was treated with silver oxide and bromine in trifluoroacetic acid. A viscous yellow oil was obtained as residue when the solvent was distilled off as previously described. Prolonged mild heating at 30° under 8 mm. pressure removed the last traces of solvent still present. On cooling the residue crystallized slowly. This material was recrystallized from carbon tetrachloride to give a 40% yield of N-bromodifluoroacetamide, m.p. 43°.

Anal. Calcd. for $C_2H_2BrF_2NO$: Br, 45.99. Found: Br, 46.01.

Bromination of Toluene.—One mole of anhydrous toluene reacted with N-bromomonochloroacetamide (0.1 mole) and then at reflux (to ensure completeness of reaction) until the mixture gave a negative test with potassium iodide solution. When the toluene mixture was cooled to 0° and filtered, 9.2 g. of solid was obtained. After recrystallization from benzene the product melted at 120°. Mixed with monochloroacetamide it melted at 120°. Distillation of the toluene filtrate first at atmospheric pressure was carried out to remove the excess toluene, then at 10 mm. pressure which yielded 11.5 g. of a fraction which distilled at 60–75°, $n^{20}D$ 1.5566.

Anal. Calcd. for C_7H_7Br: Br, 46.78. Found: Br, 46.00.

This distillate represented a 70% conversion to monobrominated toluene. Analysis with silver nitrate (alcoholic) indicated that this material contained 18% benzyl bromide. A fraction of this distillate boiling at 62–64° at 10 mm. was collected, m.p. 7.6°, $n^{20}D$ 1.5500. Five grams of this material was converted into the Grignard reagent which was carbonated with Dry Ice to give a solid acid, m.p. 172–176°. The neutralization equivalent of this acid was 133. *p*-Methylbenzoic acid melts at 179° and has a neutralization equivalent of 136. Thus, it appears that nuclear bromination occurred almost predominantly in the para position.

Similar conditions and methods of isolation were used for the entire study of the bromination of toluene by N-bromoacetamide and its halogenated derivatives. The monobrominated toluenes were isolated as described above. The results of this study are shown in Table II.

Bromination of Cyclohexene.—One mole of cyclohexene (washed with ferrous sulfate and freshly distilled) and 0.1 mole of N-bromotrichloroacetamide in several portions reacted at room temperature. After completion of the reaction, test with KI solution was found to be negative.

The solution was cooled down to 0° and 10.7 g. of white solid was filtered from the solution (A). This solid material was boiled with water for five minutes and filtered hot. On cooling the filtrate, 2.5 g. of essentially pure trichloroacetamide (mixed m.p. 140°) was obtained. The water insoluble material (7.7 g.) was recrystallized from Skellysolve C to produce 6.0 g. of white needles, m.p. 153°. This material was essentially pure N-(2-bromocyclohexyl)-trichloroacetamide.

Anal. Calcd. for $C_8H_{11}BrCl_3NO$: Br, 24.72; N, 4.32. Found: Br, 24.85; N, 4.39.

The Skellysolve filtrate was combined with the cyclohexene filtrate (A) and distilled under vacuum to remove the solvents. When the solid residue was dissolved in 100 ml. of hot Skellysolve C and allowed to cool to room temperature, approximately 0.5 g. more of the adduct (m.p. 153°) was obtained. On refrigerating the filtrate to −5°, a new solid weighing 13.0 g., m.p. 77–78°, was obtained. This material showed no unsaturation test with $KMnO_4$ solution and analysis indicated that its structure N-(2-bromocyclohexyl)-trichloroacetamide. Isomerism (*cis, trans*) was therefore postulated for the addition compound.

Anal. Calcd. for $C_8H_{11}BrCl_3NO$: Br, 24.72; N, 4.32. Found: Br, 24.92; N, 4.68.

When the final Skellysolve filtrate was fractionally distilled, a 3.0-g. of fraction boiling at 80–82° at 35 mm. was collected, $n^{20}D$ 1.5269. The material was unsaturated and silver bromide was deposited when it was treated with alcoholic silver nitrate solution. The material was considered to be 3-bromocyclohexene. Thus the reaction of N-bromotrichloroacetamide with cyclohexene gave a high melting adduct (153°) in 20% yield, a low-melting adduct (77–78°) in 40% yield, and 3-bromocyclohexene in 19% yield. Only 15% of the theoretical amount of trichloroacetamide was removed.

One mole of cyclohexene (82.0 g.) and 0.1 mole of N-bromodichloroacetamide in several portions reacted at room temperature until a negative test with KI solution was obtained. The mixture was cooled down to 0° and 6.0 g. of essentially pure dichloroacetamide (mixed m.p. 97°) was filtered off. After removal of excess cyclohexene at atmospheric pressure, distillation was continued under reduced pressure and two fractions were collected: (I) 50–110° at 8 mm.; (II) 110–128° at 8 mm. Distillation was discontinued when slight decomposition was noted. On standing, Fraction II solidified completely, whereas only about one-third of Fraction I solidified. These solids were agitated with petroleum ether to wash them free of liquid residue. After recrystallization from hot benzene both solids were observed to melt at 97–98°, mixed m.p. with dichloroacetamide (97°). Thus an additional 4.2 g. of dichloroacetamide was recovered making a total of 10.2 g. or 80% recovery. The petroleum ether fraction containing the liquid portion of Fraction I was distilled through a small helix-packed column. Twelve grams of material boiling at 69–72° at 13 mm., $n^{20}D$ 1.5285, was collected. This material gave a positive test for unsaturation with $KMnO_4$ and a positive bromine test with alcoholic silver nitrate solution. Thus this material was essentially pure 3-bromocyclohexene.

Distillation of the remainder of Fraction I gave 2.0 g. of material boiling at 102–105° at 17 mm., $n^{20}D$ 1.5520. This material gave no test for unsaturation with $KMnO_4$. When the liquid was refluxed with zinc dust and *n*-butanol for 20 minutes, a water extract of the mixture (acidified with nitric acid) gave a copious precipitate of silver bromide indicating the presence of 1,2-dibromocyclohexane. Thus the reaction of N-bromodichloroacetamide with cyclohexene produced 3-bromocyclohexene in 50% yield and 1,2-dibromocyclohexane in 15% yield. Recovery of 80% of the theoretical amount of dichloroacetamide was achieved.

The reaction between N-bromotrifluoroacetamide and cyclohexene was carried out at room temperature, after which the mixture was cooled to 0°. A white solid was obtained weighing 7.5 g., m.p. 150–154°. This material was treated with hot water and was then recrystallized from benzene, yielding 7.0 g. of a pure white solid, m.p. 156°. This solid material was saturated ($KMnO_4$ test) and analysis showed it to be essentially pure N-bromocyclohexyltrifluoroacetamide.

Anal. Calcd. for $C_8H_{11}BrF_3NO$: Br, 29.17; N, 5.11. Found: Br, 28.93; N, 5.10.

The original cyclohexene filtrate was distilled, and 2.5 g. of trifluoroacetamide (mixed m.p. 73°) sublimed as the solvent was removed. The solvent-free residue in the pot was agitated with petroleum ether. An additional 3.0 g. of white solid melting at 156° was obtained.

Distillation of the petroleum ether filtrate gave 4.0 g. of a liquid boiling at 103–107° at 18 mm., $n^{20}D$ 1.5527. As the temperature began to climb higher, decomposition occurred suddenly giving off vapors of HBr. The distillation was discontinued leaving a residual charred mass weighing 2.0 g. The distillate boiling at 103–105° at 18 mm., was a saturated compound (tested with $KMnO_4$) which upon treatment with zinc dust and 1-butanol, produced zinc bromide. Thus it appears that this compound is 1,2-dibromocyclohexane obtained in 32% conversion. The adduct N-(2-bromocyclohexyl)-trifluoroacetamide represented a 38% conversion. Trifluoroacetamide was recovered in 20% yield.

The reaction products of cyclohexene with N-bromoacetamide and N-bromomonochloroacetamide were obtained by isolation techniques similar to those described above.

Reactions with Benzyl Alcohol.—In separate experiments, 0.1 mole of the N-bromo compounds was added to 1.0 mole of redistilled benzyl alcohol at room temperature. After a short induction period, the reaction became exothermic enough to raise the temperature to the boiling point of the alcohol. During the reflux period the color changed from yellow to orange to deep red, and finally back to yellow. At this point the hot solution was tested with potassium iodide solution and no liberation of iodine was observed. The reactions were therefore considered complete. The solution was strongly acid to litmus paper due to the formation of hydrogen bromide.

The entire mixture was shaken with sodium bicarbonate solution until the evolution of CO_2 ceased. The organic layer was extracted with ether and the ether extract in turn extracted three times with 100-ml. portions of sodium bisulfite solution (30 g. per 100 ml. of water). Benzaldehyde was obtained by combining the bisulfite extracts, treating them with sodium bicarbonate until the evolution of CO_2 ceased, and steam distilling the resulting mixture. The distillate was extracted thoroughly with ether. The ether extract was dried over sodium sulfate and distilled to remove the ether. Crude benzaldehyde was obtained in 64–70% yields, b.p. 172° at 628 mm., $n^{20}D$ 1.5445. The 2,4-dinitrophenylhydrazone of this material had a melting point of 237–238°; lit. value 237°.

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Mechanisms of Elimination Reactions. V. Preparation and Elimination Reactions of *cis*- and *trans*-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene[1,2,3]

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Previous work has indicated the stereochemical preference for *trans* elimination of the elements of hydrogen halides in second-order alkaline dehydrohalogenation reactions of alkyl halides. In a continuation of a study of *cis* and *trans* elimination, work with the *cis–trans* isomers of 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene was undertaken. The isomeric compounds were prepared by diene syntheses involving anthracene with *cis*- and *trans*-dichloroethylenes. Each of the isomers gave 9,10-dihydro-9,10-ethenoanthracene when treated with sodium in isopropyl alcohol or with zinc in ethyl alcohol. The structure of the olefin was confirmed by hydrogenation to the known 9,10-dihydro-9,10-ethanoanthracene. These results show that the *trans*-configuration of halogen substituents is not required for the elimination of halogen from α,β-dihalides with metals. Each isomer was shown to give 11-chloro-9,10-dihydro-9,10-ethenoanthracene on treatment with ethanolic alkali.

A kinetic study has been made of the dehydrochlorination of each of the *cis–trans*-dichlorides with sodium hydroxide in a water–ethanol–dioxane solution at four different temperatures (30° range) for each isomer. The *trans*-dichloride (*cis*-hydrogen and chlorine atoms) unexpectedly reacted seven to nine times faster than the *cis*-dichloride (*trans*-hydrogen and chlorine atoms). To the best of our knowledge, there are no analogous results reported in the literature. This preference in rate for *cis* elimination was found to be entirely due to a favorable entropy of activation (and to the relatively high temperature required for reaction), as *trans* elimination was favored by four kilocalories per mole in activation energy. These results are discussed in terms of a planar transition state for the one-stage elimination process.

In previous papers[1b,1c] the stereochemical preference in E2 (second-order) elimination[4] of the elements of hydrogen halides from alkyl halides has been considered at length, and numerous examples have been cited where *trans* elements of hydrogen and halide are removed more readily than the corresponding *cis* elements. The superiority of *trans* elimination has been attributed[1b] to a difference in mechanism between it and the *cis* process. It was assumed that the *trans* process involved a one-stage concerted mechanism wherein the base attacks the hydrogen on the β-carbon atom, displacing the electron pair of the carbon–hydrogen bond which may simultaneously attack the α-carbon atom by a direct inversion process, forming the carbon–carbon double bond and displacing halide ion.

It was assumed that, for the concerted process, the α-carbon atom must be in position to undergo inversion in the displacement of halide by the electrons of the carbon–hydrogen bond undergoing rupture, requiring that the hydrogen and halide atoms be in *trans* position to each other. When free rotation is constrained around the carbon–carbon bond so that the hydrogen and halide atoms are *cis* to each other, the above concerted process was not deemed possible, as inversion of the α carbon atom is then not possible in the rate-determining step. It was suggested that under these circumstances the reaction then takes a course different from the one-stage process in which the base removes a proton from the β carbon atom, yielding (in the rate-determining step) a carbanion, which rapidly decomposes to olefin and halide ion.

In order to continue the work on the stereochemical aspects of dehydrohalogenation reactions, the compounds *cis*- and *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene seemed to offer an ideal system for such dehydrohalogenation studies. The usual stereochemical selectivity[5] of the diene synthesis makes it useful for the synthesis of these compounds. If the *cis* addition principle is obeyed, then condensation of anthracene with *cis*-1,2-dichloroethylene should yield *cis*-11,12-

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(2) This work was supported by the Office of Naval Research.

(3) Presented at the XIIth Congress of International Congress of Pure and Applied Chemistry, September, 1951, New York, N. Y.

(4) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(5) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).