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POSITIVE BROMINE FROM PERFLUORINATED ORGANIC BROMINE COMPOUNDS

DISSERTATION
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INTRODUCTION

The purpose of this study was to create sources of "positive" halogens from organic combinations and to investigate their reactions. "Positive" halogen means halogen bound in such a way that the bonding electrons are not shared equally by the halogen atom and its neighbor but are displaced so that the halogen has less than an equal share of the charge distribution, or, in other words, acquires a partial positive charge. In order to devise such compounds it is well first to discuss the factors which tend to prevent halogens from acting as $X^-$, favor their behavior as $X^*$ and, by extrapolation, as $X^+$.

A molecule of bromine can act as $2Br^*$ or $Br^+-Br^-$, depending on conditions; if only one reaction mode is wanted, it must be enhanced or its alternative must be repressed. For example, if toluene is treated with bromine in the cold, the bromine enters both the ring and the side chain, indicating both free radical and ionic behavior; to favor free radical bromination heat, light, or a peroxide is used, while ionic bromination is aided by Lewis acids.

In 1919 Wohl (1,2) reported an apparently general method for brominating the allyl position of an olefin. He used N-bromosuccinimide as his reagent and converted
2,3-dimethyl-2-butene into 1-bromo-2,3-dimethyl-2-butene, anisole into p-bromoanisole, and ethyl acetoacetate into its alpha-bromo derivative; in the latter case he showed that N-bromophthalimide could also be used.

After Wohl's work, little more was done on this kind of halogenation until in 1942 Ziegler (2,3), in a detailed report, showed that N-bromosuccinimide was an excellent reagent for allylic bromination. He also found that N-bromophthalimide was fairly satisfactory for this reaction, but that N-bromoglutarimide and N-bromohexahydrophthalimide could not be used.

It has been shown that N-bromosuccinimide can brominate the allyl position of olefins, that it can brominate the nucleus of aromatic and polyaromatic substances, and that it can brominate in the alpha position of ketones. Nuclear bromination of aromatics can occur in the presence of metal chlorides such as aluminum, zinc, and ferric, or sulfuric acid (2,4). Polynuclear aromatics require no catalysts: for example, naphthalene and phenanthrene give the 1- and 9-bromo derivatives respectively (2,5). Side chain bromination is favored by peroxides (2,6). Cyclohexanone and certain related compounds yield the corresponding alpha-bromoketones (2,6).

It is beyond the scope of this work to discuss reactions of N-bromoacetamide and N-bromosuccinimide in great
detail. Excellent reviews have been written on the subject as follows:


(2) Djerassi, C., Chemical Reviews 43 (2), 271 (1948)

It is generally accepted that bromination in the allyl position of olefins and the alpha position of aromatic side chains by N-bromosuccinimide or N-bromoacetamide occurs by a free radical process. If, however, N-bromosuccinimide or N-bromoacetamide is dissolved in hydroxylic solvents such as water, alcohol, or acetic acid, its bromine becomes "positive" and the elements of HOBr, ROBr, or AcOBr add across the double bond to form the bromohydrin, the 2-bromoether, or the 2-bromoalkyl acetate respectively (8,9,10,11,12). Dauben and McCoy (13) propose that N-bromosuccinimide, when dissolved in acetic acid, reacts with this solvent to give acetyl hypobromite in equilibrium with the bromoimide and say that it is this hypobromite which adds across the double bond. Extension of this postulate suggests that in ethanol the reactive species is EtOBr, and in water HOBr. A slightly different viewpoint would be the assumption that in hydroxylic solvents the N-Br bond becomes "solvated" to such an extent that it no longer breaks homolytically but rather heterolytically.
If these interpretations are correct, then N-bromosuccinimide becomes indeed a source of "positive" bromine in hydroxylic solvents. This in no way defines the bromine in N-bromosuccinimide itself as positive, however, since the molecule requires assistance to furnish this "positive" bromine. One might say, in other words, that the solvent is acting as a carrier for the bromine.

If N-bromosuccinimide is allowed to undergo reaction with olefins or alkylated aromatic compounds in an inert solvent such as carbon tetrachloride and if catalysis (either acid or peroxide) is avoided, then the intrinsic nature of the N-Br bond shows itself: it breaks homolytically. The reaction is greatly speeded up by heat and, indeed, often will not proceed at all at room temperature. An example of this heat effect is seen in the fact that N-bromosuccinimide will not react with toluene in carbon tetrachloride at the reflux temperature of the mixture (5). I have found, however, that if toluene itself is used as the solvent and the reaction carried out at its reflux temperature (110°), the reaction proceeds smoothly to give a good yield of benzyl bromide.

In alkyl bromides the bromine is present in an electronically rich state. That is, the C-Br bond exhibits properties and undergoes reactions which indicate that the bromine atom has assumed more than its statistical share of
the bonding electrons and the bond breaks heterolytically
to give Br\(^-\). Since N-bromosuccinimide gives Br\(^+\) instead of
Br\(^-\), then one might postulate that the imide residue attrac-
tion for the bonding electrons is approximately equal to
that of the bromine atom.

If this drift away from "negative" bromine is caused
by the polarizing effect of the imide ring, then added
induction should draw the bonding electrons of the N-Br
bond more strongly toward the nitrogen atom and the bromine
atom should become more "positive", and this increase in
positive character would be a measure of the effect of the
added induction over and above those effects already present
in the unsubstituted molecule. Such an additional electro-
negative effect could be supplied by replacing the alpha
hydrogens by a "negative" group such as -CN, -NO\(_2\), -CO-, 
-COO\(_R\), -C\(_2\)C-, -C\(_6\)H\(_5\), Cl, Br, or F. The effect of each of
the "negative" groups is complicated by phenomena other
than induction. However, with fluorine the complicating
features are at a minimum and it would seem to be the most
promising agent to "drain" the N-Br bond and to polarize
it in the sense \(\overset{6-}{N-Br}^{6+}\) (although not necessarily to cause
complete ionization to \(\overset{6-}{N^-}\) and Br\(^+\). However, I will here-
after refer to bromine influenced in this way as "positive"
bromine.).
The ideal grouping might well be that of N-bromohexafluorodiacetamide

\[
\begin{array}{c}
\text{CF}_3\text{CO} \\
\text{N-Br} \\
\text{CF}_3\text{CO}
\end{array}
\]

This compound could not be prepared. N-bromotrifluoroacetamide (CF_3CONHBr) might be effective, but it has only one CF_3CO- group and the induction might not be as great as one might wish. N-bromoperfluorosuccinimide (A) or N-bromoperfluoroglutarimide (B) should be very good for such a study since in these two compounds induction should be exhibited to nearly its maximum extent.

\[
\begin{array}{c}
\text{CF}_2\text{CO} \\
\text{CF}_2\text{CO} \quad \text{CF}_2\text{CO} \\
\text{N-Br} \\
\text{CF}_2\text{CO} \\
\end{array}
\]

(A) (B)

In these imides bromine is attached to a very polarizable atom of nitrogen which transmits the inductive effect from the -CF_2CO- grouping to the N-Br bond. One can include in such a system trifluoroacetyl hypobromite (CF_3CO_2Br) where the inductive effect is transmitted through a polarizable oxygen atom; the bromine in this compound should be, and is, very "positive" in character.
SCOPE

Perfluorinated N-bromoimides and perfluorinated acyl hypobromites having been chosen as most likely sources of "positive" bromine, the research problem divided itself into two parts: the preparation of these compounds, and the examination of the character of their N-Br (or O-Br) bonds.

Most of the investigations thus far reported in the literature have dealt with N-bromosuccinimide; its perfluorinated analog, N-bromoperfluorosuccinimide, was chosen for the bulk of the present study to permit direct comparisons to be made.

It has been reported (2,3) that N-bromoglutarimide is ineffective as a source of Br* in allylic bromination; its perfluorinated analog, N-bromoperfluoroglutarimide, was therefore chosen as the second reagent to see whether this anomalous behavior would persist: it did not.

N-bromotrifluoroacetamide was chosen as the third reagent to be investigated both to offer a third variation of the electronegative strength and because of its ready synthesis from trifluoroacetamide. However, the work with this compound was discontinued after it was learned that a group under Dr. Joseph Park, at the University of Colorado, was carrying out a series of investigations on electronegatively substituted N-bromoamides including N-bromo-trifluoroacetamide.
Trifluoroacetyl hypobromite (and hypolodite) was added to the study to ascertain the generality of my method of creating "positive" bromine and to obtain a qualitative comparison with the N-bromoisothiuramis. It was considered beyond the scope of the investigation to vary the electronegative group affecting the O-Br bond. While my study of trifluoroacetyl hypohalites was underway, a parallel investigation was being conducted in England by R. N. Haszeldine. Preliminary results for both his investigation and mine have already been published (14,15).

The elucidation of the character of cleavage of the N-Br (and O-Br) bond in these compounds was undertaken through an examination of the reactions which they cause. From the nature of the reaction products, the type of cleavage (homolytic or heterolytic) of the N-Br (or O-Br) bond was deduced. In order to be valid, reactions were discretely chosen and reactions were carefully controlled.

A study of the oxidizing power of these bromine compounds cannot be used to determine whether the bromine is "positive" or atomic. Since "positive" and atomic bromine both possess oxidizing abilities, the study of oxidation of various compounds, for example alcohols, by both N-bromosuccinimide and N-bromoperfluorosuccinimide might well show that identical products are formed. Moreover, oxygenated solvents such as alcohols change the character of cleavage of the N-Br bond. It is therefore desirable to eliminate
solvent effects as far as possible by choosing solvents which have little or no dipole moment and also are in themselves unreactive.

If one could devise a reaction which was obviously ionic in nature and which could be studied in an inert non hydroxylic solvent in the absence of catalysis, then such a reaction could be used to differentiate between homopolar and heteropolar cleavage of the N-Br bonds in these compounds. Such an ideal reaction would seem to be realized in the reaction of the N-bromoimides with a neutral salt such as NaCl in an inert solvent. Those N-bromoimides in which the N-Br bond is homopolar in character should not react with NaCl, whereas those in which the N-Br bond is heteropolar should react to yield Br-Cl. Moreover, if two such N-bromoimides reacted with NaCl, but at different rates, then if steric factors were equal one could infer that the more active N-bromoimide had a N-Br bond which possessed a greater degree of polar character than the less reactive compound.

Another test of reactivity of the N-bromoimides which might be considered decisive in showing the polar cleavage of the N-Br bonds is that of uncatalyzed bromination of toluene. When toluene is reacted with bromine or N-bromoimides, two types of substitution are possible, nuclear or side chain, depending on the conditions used. If the reaction is carried out in the dark in the presence of a carrier such
as ferric chloride (ionic substitution conditions) bromination occurs in the ortho and para positions exclusively \((2,4,16)\). If, however, the reaction is carried out in the presence of heat, light, and/or a peroxide catalyst (conditions for free radical substitution) then substitution occurs exclusively in the side chain \((2,6,16)\). Toluene would therefore seem ideally suited to test whether N-bromoimides react spontaneously through a free radical or ionic process. The toluene should serve well as its own solvent because of its insignificantly low dipole moment. The ratio of bromotoluene to benzyl bromide should afford an excellent measuring stick for the elucidation of the degree of polar cleavage of the various N-Br bonds. Furthermore, a kinetic study of the bromination of toluene also would contribute greatly to the knowledge concerning the character of cleavage of the N-Br bond.

There is yet another reaction whose study would increase the knowledge concerning the character of cleavage of the N-Br bond. This is the reaction of N-bromoimides with olefins. It is widely accepted that allylic bromination of olefins proceeds by a free radical process. Although N-bromosuccinimide reacts readily with olefins under the influence of heat, light, or peroxides \((2)\) to brominate in the allyl position, it does not add to the double bond, yet free radical addition would be easy to
visualize. That N-bromosuccinimide does not add would seem to indicate that free radical attack of olefins occurs preferentially at the allyl position. If, in contrast, the perfluorinated N-bromomides could be shown to add to the double bond, this could be regarded as a further piece of evidence for characterizing the reaction behavior of such N-Br bonds as ionic.

The reaction of an N-bromoimide to an olefin could conceivably occur through a molecular addition simultaneously to both carbon atoms of the bond, in which case the addition would be expected to be cis. However, it is beyond the scope of this investigation to attempt to learn whether cis or trans addition occurs.
RESULTS

N-bromoperfluorosuccinimide

N-bromoperfluorosuccinimide was prepared from the imide in high yield (86%) and in high purity (99.56%) by the use of silver trifluoroacetate and bromine in trifluoroacetic acid.

N-bromoperfluorosuccinimide has been shown to react with toluene at room temperature to brominate exclusively in the ring. Under the same conditions, N-bromosuccinimide was shown to react not at all, and bromine was shown to give an appreciable amount of benzyl bromide. At 90°, N-bromoperfluorosuccinimide brominates toluene to produce about half as much benzyl bromide as bromotoluene; N-bromosuccinimide and bromine, reacted with toluene under the same conditions, gave high yields of benzyl bromide. These data are interpreted to mean that the three brominating agents must be placed in the order N-bromoperfluorosuccinimide, bromine, N-bromosuccinimide with respect to their abilities to effect ionic (nuclear) bromination of toluene.

N-bromoperfluorosuccinimide did not brominate benzo-trifluoride or benzoic acid, whereas it did brominate toluene under the same conditions. This indicates in a qualitative way the brominating power of the reagent.

It has been shown that N-bromoperfluorosuccinimide will oxidize benzyl alcohol and benzaldehyde to benzaldehyde and benzoic acid in high yields respectively, ethanol
to acetic acid and other products, isopropyl alcohol to acetone (and bromoacetone) and n-propanol and cyclohexanol to unidentified carbonyl compounds.

N-bromoperfluorosuccinimide was reacted with cyclohexene to give an 80% yield of the adduct, which was the sole product isolated.

Reactions of both N-bromoperfluorosuccinimide and N-bromosuccinimide with inorganic reagents such as AgNO₃, AgNO₃, KI, KBr, and NaCl show that both N-bromoimides behave in essentially the same way (although the unfluorinated N-bromoimide is slower) in aqueous solution. In dry acetonitrile, however, the fluorinated N-bromoimide reacts with solid NaCl to form BrCl, whereas the unfluorinated N-bromoimide does not. Thus, while the two bromoimides react similarly in aqueous solution to indicate in both cases that the bond splits heterolytically, when one shifts to a nonaqueous solvent such as acetonitrile the unfluorinated analog loses its ability to oxidize Cl⁻, whereas the fluorinated bromoimide does not. This is interpreted to mean that in this reaction the N-Br bond in the fluorinated bromoimide is much more highly ionic than the one in the unfluorinated analog.

From the kinetic study of the bromination of toluene with N-bromoperfluorosuccinimide it was found that fresh N-bromoperfluorosuccinimide reacts initially with toluene
in acetonitrile at 25° according to the following (approximate) second order kinetic expression

\[-\frac{dc}{dt} = 7 \times 10^{-5}c_1c_2\]

where \(c_1\) and \(c_2\) are the concentrations of N-bromoperfluorosuccinimide and toluene. This kinetic law is the one which would be followed if the bromoimidide and the toluene reacted together as isolated molecules unaffected by environmental conditions other than solvent effects. It was further shown that after reaction has occurred to an appreciable extent it becomes complex and the overall rate slows down faster than would be predicted from the above kinetic equation.

It was further shown that bromotoluene has no effect on the reaction, whereas the presence of water causes a distinct, though moderate, increase in the overall rate. Furthermore, N-bromoperfluorosuccinimide which has stood for 10 days at 25° in an acetonitrile solution exhibits greatly increased reactivity over that of a freshly prepared solution.

All of the foregoing results, including the reaction of N-bromoperfluorosuccinimide with alcohols and aldehydes (and ketones), with cyclohexene, with the various inorganic reagents, with toluene, and the kinetics of the initial reaction with toluene are consistent with heterolytic cleavage of the N-Br bond. Indeed, the reaction with NaCl in acetonitrile, with toluene, and the kinetics of the
reaction with toluene seem to preclude the possibility of a radical chain mechanism. It is therefore concluded that the N-Br bond in N-bromoperfluorosuccinimide has a high degree of ionic character at room temperature and in a non-polar solvent. As the temperature is raised the bond becomes less polarized and more inclined to split homolytically.

**N-bromoperfluoroglutarimide**

N-bromoperfluoroglutarimide was prepared in an 89% yield and in a purity of 89% by the use of silver trifluoroacetate and bromine in trifluoroacetic acid.

During one preparation of N-bromoperfluoroglutarimide an unusual side reaction was obtained which resulted in a 15% yield of omega-bromohexafluorobutyramide along with the expected N-bromoimide.

In the reactions investigated, (that is in the bromination of toluene and the reaction with AgNO₂, AgNO₃, KI, KBr, and NaCl) N-bromoperfluoroglutarimide reacts in a manner very similar to that of N-bromoperfluorosuccinimide: that is a contrast to the unfluorinated imides, where N-bromosuccinimide is a brominating agent while N-bromoglutarimide is not.

**N-bromotrifluoroacetamide**

N-bromotrifluoroacetamide has been prepared in 70% yield and 96% purity. Both ethyl acetate and trifluoro-
acetic acid have been used successfully as solvents for its preparation. This bromoamide reacts incompletely with aqueous KI in neutral solution, but reacts quantitatively with KI in acid solutions. It also liberates bromine from aqueous KBr and does not react with aqueous AgNO₃.

N-bromotrifluoroacetamide was reacted with cyclohexene to yield the adduct, another high melting solid which was not identified, and a liquid fraction which also was not identified. This work was discontinued when it was learned that Dr. Joseph Park's group at the University of Colorado was investigating the same reagent.

**Trifluoroacetylhypochlorites**

The silver trifluoroacetate-halogen method of halogenation developed during this investigation (trifluoroacetyl hypochlorite) has been used to iodinate toluene to give an 84% yield of iodotoluene consisting predominantly of the para isomer, to brominate toluene with a 73% yield of mainly p-bromotoluene, to brominate beta-methylnapthalene to yield 60% alpha-bromo-beta-methylnapthalene, and has been shown to be inert toward benzotrifluoride at room temperature. The method also was used in an attempt to brominate ethyl n-butyrate. At room temperature no reaction occurred, and at reflux an unknown reaction occurred which used up all the silver salt while leaving an excess of bromine.
Miscellaneous Reactions

Both perfluorosuccinimide and perfluoroglutarimide have been shown to react with water to open the ring and form the corresponding half amide acid.

Perfluorosuccinimide was reacted with diazomethane to give a product which, though analysis for nitrogen gave an incorrect value, was considered to be N-methylperfluorosuccinimide. This same substance was synthesized by cyclizing N,N'-dimethylperfluorosuccindiamide in 95% H₂SO₄.

An incidental observation followed by more detailed work resulted in the reaction of trifluoroacetic acid with cyclohexene to give an 87% net yield of cyclohexyl trifluoroacetate, a previously unreported compound.
THE EXPERIMENTATION

I. N-BROMOPERFLUOROSUCCINIMIDE

A. Preparation of Perfluorosuccinimide

1. The Preparation of Perfluorosuccinic Acid. In the early stages of this work (17) perfluorosuccinic acid was prepared by the sequence (18):

\[
\begin{align*}
1. \text{CHCl}_2\text{-CCl}_3 & \xrightarrow{\text{SbF}_3} \text{CHCl}_2\text{-CClF}_2 \quad \text{Conversion Reference } \text{SbF}_3 \text{Cl}_2 (55\%-60\%) \quad (19,20) \\
2. \text{CHCl}_2\text{-CClF}_2 & \xrightarrow{25\% \text{ aqueous KOH}} \text{CCl}_2\text{-CF}_2 \quad (75\%-80\%) \quad (19) \\
3. \text{CCl}_2\text{-CF}_2 & \xrightarrow{\text{heat and pressure}} \text{CF}_2\text{-CCl}_2 \quad (80\%-85\%) \quad (21) \\
4. \text{CF}_2\text{-CCl}_2 & \xrightarrow{\text{zinc in alcohol}} \text{CF}_2\text{-CCl} \quad (90\%-95\%) \quad (18) \\
5. \text{CF}_2\text{-CCl} & \xrightarrow{\text{alkaline } \text{KMnO}_4} \text{CF}_2\text{-CO}_2\text{H} \quad (65\%-70\%) \quad (18)
\end{align*}
\]

The reported yields were closely duplicated. Later a simplification of the first two steps was devised (1' and 2') and the last step was carried out in aqueous acetone instead of water (5').

\[
\begin{align*}
1'. \text{CF}_2\text{H-CH}_3 & \xrightarrow{4\text{Cl}_2 \text{ uv}} \text{CF}_2\text{Cl-CCl}_3 \quad \text{(quantitative)} \quad (22) \\
2'. \text{CF}_2\text{Cl-CCl}_3 & \xrightarrow{\text{zinc in alcohol}} \text{CCl}_2\text{-CF}_2 \quad (90\%-95\%) \\
5'. \text{CF}_2\text{-CCl} & \xrightarrow{\text{KMnO}_4 \text{ in cold acetone}} \text{CF}_2\text{-CO}_2\text{H} \quad (74\%)
\end{align*}
\]

The starting material, \text{CF}_2\text{HCH}_3, is commercial; it is very cheap; it has the fluorine atoms in the right place; and its chlorination and dechlorination are essentially quantitative.
Chlorination of CF₂H-CH₃ to CF₂Cl-CCL₃ (22): A five gallon glass carboy was filled with water and connected by a siphon to a second empty carboy. The first carboy, illuminated by a General Electric Sunlamp was charged with "Genetron 100" (CHF₂CH₃) and chlorine in about a one to five ratio until about two thirds of the water had been displaced by the gas mixture. The "Genetron 100" and the chlorine were continuously fed to the carboy at a rate such that the water level neither rose nor fell as the chlorination proceeded. Since CF₂Cl-CCL₃ is denser than water and insoluble, it sinks immediately while the HCl formed dissolves in the water. The rate of feed needs adjustment only occasionally after equilibrated conditions are approximately reached. The water eventually becomes saturated with HCl and must be replaced. The tetrachlorodifluoroethane is siphoned off occasionally, dried, and rectified by simple distillation.

Dehalogenation of CF₂Cl-CCL₃ to CF₂=CCl₂: CF₂Cl-CCL₃ (101 grams, 0.5 mole) was dissolved in 300 ml of absolute alcohol, and this solution was added dropwise to granular zinc (35 grams, 0.55 mole) covered by absolute alcohol in a one liter flask equipped with a reflux condenser attached to a Dry-Ice-acetone trap. Spot heating started the reaction, which then proceeded spontaneously. The yield of CF₂=CCl₂ was 62.6 grams (0.47 mole, 94% theoretical).

Dimerization of CF₂=CCl₂: CF₂=CCl₂ (400 grams, 3.0 moles) was placed in a one liter steel bomb and heated with shaking
at 225° for 24 hours. The bomb was cooled and opened, and the product was dissolved out of the bomb with ether. Distillation yielded the cyclobutane (336 grams, 2.52 moles, 84% theoretical) boiling range 129-131°.

Dechlorination of CCl₂-CCl₂-CF₂-CF₂: The cyclobutane (100 grams, 0.376 mole) was dissolved in absolute alcohol, and the solution was added dropwise to granular zinc (27 grams, 0.41 mole) covered by absolute alcohol in a one liter three necked flask equipped with reflux condenser and dropping funnel. After spot heat starting, the reaction became spontaneous. After all the cyclobutane had been added and the reaction had slowed down, the flask was heated to a moderate reflux overnight. The cyclobutene was distilled off as an azeotrope with alcohol, b.p. 58°, washed, decanted, dried, and distilled. A 95% yield of CF₂CF₂CCl=CCl, b.p. 63-64°, was obtained.

Oxidation of CF₂CF₂CCl=CCl to Perfluorosuccinic Acid: For large scale operation, oxidation with aqueous permanganate is best, but for small scale operation, oxidation with an aqueous-acetone solution of permanganate is faster and gives a better yield. The aqueous acetone method should be used only on a small scale for two reasons: first, potassium permanganate is rather insoluble in such a solvent and second, there is the distinct danger that the reaction might escape control by oxidation of the acetone itself in which case the reaction becomes violent and
almost explosive. However, with small amounts and adequate cooling the reaction proceeds quite smoothly.

In a typical experiment, KMnO₄ (29.0 grams, 0.138 mole) dissolved in a minimum amount of acetone containing 10% by volume of water was added dropwise to the cyclobutene (24.5 grams, 0.125 mole) which had been dissolved in acetone in a one liter three necked flask fitted with condenser, stirrer, and dropping funnel. An exothermic reaction proceeded, and the solution was kept at a temperature below 25° by means of an ice bath. When the addition of the permanganate had been completed the solution was colorless, indicating a deficiency of permanganate, so more KMnO₄ (11.0 grams) was added. This was an excess. The excess permanganate was destroyed with SO₂, and the MnO₂ was filtered off leaving a colorless filtrate. The acetone was distilled off, and the remaining acid-water solution was continuously extracted with ether for three days. Removal of the ether and distillation of the residue gave 17.5 grams (73.6% yield) of perfluorosuccinic acid, boiling range 135-140°.

2. Preparation of Perfluorosuccinimide from Perfluorosuccinic Acid: Perfluorosuccinic acid was converted into its imide as follows (17, 23):

\[
\begin{align*}
\text{CF}_2\text{CO}_2\text{H} &+ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{quantitative} \text{CF}_2\text{CO}_2\text{Et} \\
\text{CF}_2\text{CO}_2\text{H} &+ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{quantitative} \text{CF}_2\text{CO}_2\text{Et}
\end{align*}
\]
The Esterification of Perfluorosuccinic Acid: Perfluorosuccinic acid was quantitatively esterified (17,18,23) by refluxing it with a mixture of ethanol and benzene, removing the water as a ternary azeotrope as it was formed. Vacuum distillation gives diethyl perfluorosuccinate, b.p. 94-97° at 20 mm., $n_2^2 1.3659$.

The Ammonolysis of Diethyl Perfluorosuccinate: The ammonolysis was carried out in a conventional manner (17,23,24). Diethyl perfluorosuccinate (370 grams, 1.50 moles) and one liter of diethyl ether were placed in a two liter Erlenmeyer flask and cooled in ice. Dry ammonia was bubbled through the solution from a glass tube extending to the bottom of the flask. After two hours the amide was filtered off to give, after drying, 273.0 grams of white powder. The ether solution was evaporated to a small volume and a second crop of 4.9 grams of powder was obtained. The two crops were combined to give, after washing with ether and drying, 278 grams (1.48 moles, 98.6% theoretical) of white, powdery perfluorosuccindiamide, m.p. 254-256° (uncorrected). When recrystallized from dioxane a melting point of 259.8 to 260.3° was obtained (17,23).

Cyclization of Perfluorosuccindiamide to Perfluorosuccinimide: The method reported earlier (17,23) for the conversion of the diamide to the imide involved combining
the amide with 95% sulfuric acid and heating under reduced pressure for an 80% conversion, 94% net yield. Later experiment showed that hot 95% sulfuric acid causes a partial hydrolysis of the amide with a consequent loss of conversion. When 100% acid was used, the yield became almost quantitative.

The 100% sulfuric acid was prepared by combining 450 grams of 95% sulfuric acid with 333 grams of 30% fuming sulfuric acid (oleum). In one experiment perfluorosuccindiamide (596 grams, 3.17 moles) was combined with 100% sulfuric acid (311 grams, 3.17 moles) in a one liter modified Claisen flask fitted with a water cooled solids receiver and connected through a Dry-Ice trap to a vacuum pump. The flask was heated with a free flame until a clear solution was obtained. The flask was allowed to cool slightly and vacuum was slowly applied down to 40 mm. As much material as possible was distilled over at 40 mm. by heating with a free flame through a wire gauze; then the pressure was lowered to 15 mm. and the distillation continued until foaming in the flask interfered. The distillate weighed 531 grams. This crude was then redistilled through the same apparatus, but with an oil bath as the heat source, to give white, solid perfluorosuccinimide (509 grams, 2.97 moles, 94.0% theoretical) b.p. 83-93° at 20 mm. (mostly at 88°), neutral equivalent 170 (theoretical is 171).
B. Preparation of N-bromoperfluorosuccinimide

1. Methods of Bromination which Failed: Several methods were tried unsuccessfully for the bromination of perfluorosuccinimide including:

   a) direct bromination with bromine in CCl₄
   b) direct bromination with bromine and red phosphorus in CCl₄
   c) treatment with cold aqueous NaOH and bromine
   d) treatment with sodium acetate (aqueous) and bromine
   e) treatment with N-bromosuccinimide in CCl₄

That the first two methods failed is not surprising, since it was subsequently learned that N-bromoperfluorosuccinimide reacts instantly with HBr to produce bromine and perfluorosuccinimide.

The failure of methods c) and d) are readily understandable in light of later experiments which have shown that not only is perfluorosuccinimide very rapidly hydrolyzed in aqueous base, but that it is even quickly hydrolyzed in pure water at room temperature.

In an attempt to prepare N-bromoperfluorosuccinimide by reacting perfluorosuccinimide with N-bromosuccinimide, the two were mixed in equal molar proportions and refluxed in CCl₄ overnight. It was then found that the reaction mixture gave no test for available bromine (negative aqueous iodide test) and no test for bromide ion (no precipitate with alcoholic silver nitrate). Insoluble succinimide was
removed from the top of the hot CCl₄. On cooling the solution, a white crystalline solid was obtained which on sodium fusion tested for fluorine and nitrogen but not bromine and had a neutral equivalent of 260 and a melting point of 80.0 to 81.5°. On evaporation of the supernatant CCl₄ to a small volume (the solution was strongly lacrimatory) a yellow oil was obtained which, on sodium fusion, tested for fluorine, bromine, and nitrogen. No further attempt was made to identify these products.

2. Successful Methods of Brominating Perfluorosuccinimide: Successful results were obtained by treating the imide in a suitable solvent with a silver salt such as silver nitrate, or preferably silver trifluoroacetate, and bromine.

The Use of Silver Oxide: Early work was done in which perfluorosuccinimide was treated with an aqueous suspension of silver oxide to prepare what was considered its N-silver derivative which was then treated with bromine in a suitable solvent. After the effect of water on the imide was discovered (see section V) this practice was discontinued because the substance thought to be the N-silver imide almost certainly was the silver salt of the half amide of perfluorosuccinic acid. For the same reason the practice of dissolving silver oxide in trifluoroacetic acid, adding the imide and then bromine was also discontinued because the reaction of silver oxide with trifluoroacetic acid produces half a mole of water per mole of acid.
The Use of Silver Trifluoroacetate: Silver trifluoroacetate was found best as a source of silver ion. It is not sensitive to light; it forms only silver bromide and trifluoroacetic acid during bromination; and it is very soluble in a wide variety of organic solvents.

The Choice of Solvent: In the silver salt method of halogenation, the silver salt, (preferably silver trifluoroacetate,) is combined with the imide in a suitable dry, inert solvent and bromine is added to the mixture. Silver bromide is precipitated almost instantly and is removed by filtration. The bromoimide is then isolated by evaporation of the solvent.

Diethyl ether, ethyl acetate, acetonitrile, and trifluoroacetic acid were used successfully as solvents. However, from all of these solvents except trifluoroacetic acid, the yields have been low and the solvents formed on evaporation viscous and difficultly crystallizable syrups containing partly brominated solvent. Trifluoroacetic acid, however, is immune, and the bromoimide can be prepared in this solvent in good yield.

The Recommended Method - Silver Trifluoroacetate in Trifluoroacetic Acid: Perfluorosuccinimide (214 grams, 1.25 moles) and silver trifluoroacetate (276 grams, 1.25 moles) were dissolved in 1093 grams of trifluoroacetic acid of better than 99% purity in a two liter three necked flask fitted with thermometer, all-glass stirrer, and dropping
funnel. In 15 minutes bromine (200 grams, 1.25 moles) was added dropwise while the temperature was kept between 15 and 20° by an ice bath. Stirring was maintained for another hour. Filtercell was added and the mixture was filtered through a filter consisting of a glass column about four inches in diameter and one foot high, fitted at the bottom with a standard taper male joint over which fitted a female joint the opening of which was covered with a perforated glass disk. This disk was covered with a pad of glass wool and then a half-inch layer of fine sea sand. A filter paper disk was placed over the sand to prevent displacement by splashing. This apparatus and the reaction flask were flushed out with dry nitrogen before use to displace the air.

After the mixture was filtered (transfer of the mixture from reaction flask to filter was accomplished through a flexible rubber and glass tube) the filter and the reaction flask were washed with 320 grams of trifluoroacetic acid. This made the total amount of trifluoroacetic acid used 1413 grams. The filtrate was collected in a three neck flask as a red-brown bromine colored solution. Boiling chips were added. One small neck and the large neck were stoppered (a three neck flask was used so that the resulting solid bromoimide could more readily be removed). To the other neck was fitted a large Dry-Ice cold finger condenser filled with ice and water. This was connected
through three Dry-Ice traps to a vacuum pump. The tri-
fluoroacetic acid was distilled off at 20 mm., at which
pressure it boils at approximately -20°. When the last of
the solvent was distilled off the material remaining in
the flask solidified to a white crystalline solid. The
recovered acid was rectified to give 1186 grams (83.9%
recovery) of trifluoroacetic acid (some of the acid was
lost as a result of accidental spillage during recovery).

The white crystalline solid N-bromoperfluorosuccin-
imide was transferred to a 250 ml round bottom standard
taper flask. This flask was attached to the Dry-Ice cold
finger condenser used before, which in this case was used
as a sublimate condenser surface. The solid was sublimed
at three mm. pressure with a water bath at 50 to 60° to
heat the flask. N-bromoperfluorosuccinimide (267.5 grams,
1.07 moles, 85.6% theoretical) was obtained as a white
crystalline solid, m.p. 49.5 to 50.5°, which contained
31.82% active bromine by potassium iodide-sodium thiosulf-
ate titration (theory is 31.96% bromine). This indicates
a purity of 99.56%. There remained at the end of the sub-
limation 17 grams of a white powder which contained 21.4%
active bromine. This was soluble in water, had only a trace
of silver ion present, and melted higher than the bromo-
imide. This material probably contained any or all of
the following: 1) perfluorosuccinimide, 2) the half amide
of perfluorosuccinic acid, or 3) the N-bromo derivative
of the half amide of perfluorosuccinic acid. These compounds would result from the presence of small amounts of moisture or from incomplete reaction.

In the recommended procedure trifluoroacetic acid is used as a solvent. Its main advantages are a) it has a convenient boiling point (72°) far different from that of the other reactants and products, b) it is completely inert in this reaction (at least in its over all aspect; the reaction might well proceed through the transient formation of trifluoroacetyl hypobromite), and c) there is no difficulty in separating the solvent from the product, since difficultly crystallizable syrups do not form on distillation to small volume.

C. Reactions of N-bromoperfluorosuccinimide

After completing the preparation of N-bromoperfluorosuccinimide the problem of determining the character of its N-Br bond was undertaken. The expectation was that, by induction, the bromine would be electronically drained to the point of becoming positive and not merely neutral as in unfluorinated N-bromoimides. Reactions were therefore sought which would give a contrast between the fluorinated and the unfluorinated imides.

1. Reaction with Toluene: N-bromoperfluorosuccinimide was reacted with toluene under various conditions in order to determine whether the N-Br bond splits homolytically or heterolytically. Bromine and N-bromosuccinimide were also
reacted with toluene under the same conditions to serve as a basis for comparison.

**Bromination of Toluene with N-bromoperfluorosuccinimide**

at 24°: N-bromoperfluorosuccinimide (12.5 grams, 0.05 mole) was added to 50 ml of toluene in a 500 ml flask fitted with thermometer, stirrer, and reflux condenser and maintained at 24°±1° in the dark by means of a water bath. The reaction was followed by iodimetric titration and was stopped after 16 hours when it was found that only 0.0013 mole of the bromoimide remained unreacted. A total of 5.0 ml (10%) of the solution was used for analyses. A one ml aliquot of the reaction mixture was treated with an excess of alcoholic silver nitrate and the available bromine content was determined gravimetrically to be 0.0020 mole. Thus there was only 0.0007 mole of bromine present in the reaction mixture as bromine, bromide, or benzyl bromide. The reaction mixture was diluted with ether, washed with a bisulfite solution and then water, and dried. The ether was evaporated and the remaining liquid distilled to give, after removal of the toluene, a milky distillate distilling from 155 to 180° which deposited a crystalline solid on cooling. The distillate was diluted with petroleum ether (b.p. 30 to 60°) which precipitated the solid. This was filtered, washed with petroleum ether, and dried to yield crude perfluorosuccinimide, m.p. 64-67°. It is thus obvious that the original extraction had been incomplete.
The petroleum ether was re-extracted with sodium bicarbonate solution and water and dried over sodium sulfate, after which the petroleum ether was removed and the remaining material distilled to yield monobrominated toluene (4.8 grams, 56% theoretical) distilling at 180 to 185°, n_D^20 1.5500, freezing point 5.5°. Since 10% of the reaction mixture was used in analyses, then the corrected yield was 62%. The product had no odor of benzyl bromide. Gravimetric analysis of this product showed that it contained 0.3% of available bromine calculated as benzyl bromide.

**Bromination of Toluene with N-bromosuccinimide at 25°:**
N-bromosuccinimide (8.9 grams, 0.05 mole) was added to 50 ml of toluene in the same apparatus that was used before and maintained at 25°±1°. The contents were stirred in the dark for 16 hours. At the end of this time the solid remaining in the toluene was filtered off and washed with petroleum ether to yield 8.3 grams of a solid which gave strong evidence of bromine when tested with aqueous potassium iodide. The toluene solution, diluted with petroleum ether, was washed with bisulfite solution, sodium bicarbonate solution, then water, dried, and evaporated to small volume. The toluene was distilled off without giving any higher boiling material. This indicated that under these conditions N-bromosuccinimide had not reacted with toluene.

**Bromination of Toluene with Bromine at 25°:** Bromine (8.0 grams, 0.05 mole) was added to 50 ml of toluene in the same
apparatus used before and maintained at $25^\circ \pm 1^\circ$. After the reaction had proceeded in the dark for 16 hours the solution was diluted with petroleum ether (b.p. 30-60°), washed with bisulfite solution, sodium bicarbonate solution, and then water, and dried over sodium sulfate. The petroleum ether was removed along with the toluene, and then a fraction was collected from 180 to 185° which was monobrominated toluene (1.4 grams, 0.008 mole, 16% theoretical). Gravimetric analysis of the product showed that it contained 6.4% available bromine (as benzyl bromide).

Bromination of Toluene with N-bromoperfluorosuccinimide at 90°: N-bromoperfluorosuccinimide (12.5 grams, 0.05 mole) was reacted with 50 ml of toluene at 90° in the dark rather than at 25° and for 20 minutes rather than for 16 hours. The product was worked up as previously described and distilled to give monobrominated toluene (6.2 grams, 0.036 mole, 72% theoretical) b.p. 180 to 210°. Gravimetric analysis of the brominated product showed that it contained 34.7% of benzyl bromide.

Bromination of Toluene with N-bromosuccinimide at 90°: N-bromosuccinimide (8.9 grams, 0.05 mole) was reacted with 50 ml of toluene in the dark at 90° for 10 hours. The mixture was worked up as described before to give monobrominated toluene (6.8 grams, 0.04 mole, 80% theoretical) b.p. 196 to 201°. Gravimetric analysis showed that it contained 97% benzyl bromide.
Bromination of Toluene with Bromine at 90°: Bromine (8.0 grams, 0.05 mole) was reacted with 50 ml of toluene at 90° in the dark. The reaction was complete after one hour as evidenced by complete loss of bromine color. The mixture was worked up as previously described and distilled to give monobrominated toluene (6.4 grams, 0.038 mole, 76% theoretical), b.p. 193 to 203°. Gravimetric analysis of the product showed that it contained 84.9% benzyl bromide.

Bromination of Toluene with N-bromoperfluorosuccinimide Under Mixed Conditions: To 50 ml of toluene in a 100 ml flask fitted with reflux condenser was added N-bromoperfluorosuccinimide (25.0 grams, 0.10 mole). Heat of reaction was noted along with the formation of a deep amber coloration. When the initial reaction had subsided (about 15 minutes), the mixture was heated to reflux in the dark. On reaching the reflux temperature the color disappeared, but reflux was continued for one-half hour. Dense white fumes of HBr were noted when the flask was opened. The solution was washed well with water and dried over sodium sulfate. Monobrominated toluene (13.4 grams, 78.4% theoretical), b.p. 170 to 182° was collected on distillation. The odor of benzyl bromide was observed. Gravimetric analysis showed that the product contained 7.7% benzyl bromide.

Bromination of Toluene with N-bromosuccinimide at Reflux: To 50 ml of toluene in a flask fitted with reflux condenser was added N-bromosuccinimide (10.0 grams, 0.056 mole).
The mixture was heated to reflux for 10 hours in the dark. It was then cooled and the succinimide filtered off, after which the filtrate was distilled to give benzyl bromide (6.2 grams, 0.036 mole, 64% theoretical), b.p. 200°. Analysis of the product showed that it consisted of 100% benzyl bromide.

**Bromination of Toluene with Bromine under Mixed Conditions:**

Bromine (32.0 grams, 0.20 mole) was added to 50 ml of toluene in a glass flask fitted with reflux condenser which had a water trap attached to its opening to collect the HBr evolved. The mixture was allowed to react at will in the dark for 15 minutes after which it was heated to reflux for one-half hour, at which time the reaction was complete. The product was worked up to give monobrominated toluene (25.0 grams, 73% theoretical) b.p. 180 to 210°. Gravimetric analysis showed that the product contained 36.6% benzyl bromide.

The foregoing results are summarized in Table I. It can be seen readily from the table given below that the three brominating agents must be placed in the order N-bromoperfluorosuccinimide greater than bromine which is very much greater than N-bromosuccinimide with respect to their abilities to effect nuclear (i.e., ionic) bromination of toluene.
2. Attempt to Brominate Benzotrifluoride: The N-bromoperfluorosuccinimide used in this experiment was prepared in diethyl ether as the solvent, was no better than 64% in purity, and was probably contaminated with higher boiling brominated derivatives of ether.

This crude N-bromoperfluorosuccinimide (157 grams of 64% pure material, 0.4 mole) was added to benzotrifluoride (66 grams, 0.45 mole). The clear, brownish tinted solution was allowed to stand at room temperature in the dark. Iodimetric titrations of aliquots of this solution taken at the beginning and end of this time showed that there had been no loss of active bromine. Therefore, N-bromoperfluorosuccinimide may be said not to react detectably with benzotrifluoride in 46 hours at room temperature.

The above mixture was refluxed for 22 hours in the
dark. Aliquot portions titrated at the beginning and end showed that 28% of the active bromine content had been lost. The solution had become darker, but no bromine was collected in a Dry-Ice trap connected to the condenser outlet. The resulting mixture was washed with bisulfite solution and then with water and dried over CaCl₂. This material was distilled at 4 mm. pressure to give recovered benzotrifluoride and a clear distillate, b.p. 50 to 88° at 4 mm. This material fumed in air, darkened on standing, and gave quick precipitates of AgBr with both aqueous and alcoholic AgNO₃. It is thus to be concluded that this high boiling fraction, containing labile bromine, is derived not from benzotrifluoride but from impurities present in the original N-bromoperfluorosuccinimide sample which was used and probably contained brominated ether.

3. The Oxidation of Benzyl Alcohol: N-bromoperfluorosuccinimide (2.5 grams, 0.0095 mole) of 95% purity was added to an excess (20ml) of benzyl alcohol. Only slight heating effect was noticed. After standing for one hour at room temperature, the reaction was not completed, so the mixture was warmed on a hot plate until completion occurred (within two minutes). The odor of benzyl bromide was noted. The 2,4-dinitrophenylhydrazone was prepared according to the method of Shriner and Fuson (25). This derivative was recrystallized from a mixture of ethyl acetate and acetone to give the 2,4-dinitrophenylhydrazone of
benzaldehyde (2.4 grams, 0.084 mole, 88.5% theoretical) m.p. 235 to 236°.

4. The Oxidation of Benzaldehyde: N-bromoperfluorosuccinimide of 95% purity (5.0 grams, 0.019 mole) was added to an excess (10 ml) of benzaldehyde. No observable reaction occurred at room temperature, so the solution was heated on the steam bath. After an induction period of about two minutes a sudden reaction started which boiled the solution and which was accompanied by the transient appearance of a bromine coloration. This solution was cooled, diluted with ether, and extracted with dilute aqueous NaOH. The NaOH solution was washed well with ether and acidified with dilute sulfuric acid. The solid which precipitated from solution was extracted with ether, and the ether solution was dried over CaCl₂ and then evaporated to dryness to give 3.3 grams of a tan solid which was strongly acidic. This material was recrystallized from 50 ml of hot water to give, after drying, benzoic acid (1.9 grams, 0.0157 mole, 82% theoretical) as shiny plates, m.p. 120 to 121°. It is probable that the first solid (3.3 grams) was a mixture of benzoic acid and perfluorosuccinic acid which resulted from the base catalyzed hydrolysis of the perfluorosuccinimide.

5. Attempt to Brominate Acetic Acid: When N-bromoperfluorosuccinimide was added to an excess of glacial acetic acid no observable reaction occurred at room temperature
and the mixture formed a water white solution. On heating to reflux temperature, however, the solution became darkly colored with bromine. Distillation of this mixture gave only acetic acid and bromine and a tarry residue. No brominated products were isolated.

6. Miscellaneous Small Scale Reactivity Experiments:

**Benzene:** Benzene shows little tendency to react with N-bromoperfluorosuccinimide as shown by the fact that one gram of the bromoimide mixed with an excess (20 ml) of benzene did not lose its reactivity after standing for 26 days at room temperature and in the dark. (The bromoimide is only slightly soluble in benzene.)

**Acetonitrile:** In another experiment one gram of the bromoimide, dissolved in an excess (about 20 ml) of acetonitrile and kept at room temperature in the dark for 13 days, lost none of its active bromine content according to aliquot iodimetric titrations. In 26 days the solution had lost only 4.2% of its active bromine content.

**Ethyl Acetate:** In a third experiment one gram of the bromoimide, dissolved in about 20 ml of ethyl acetate and kept at room temperature in the dark, lost 8.2% of its active bromine content in 13 days and 23% after 26 days.

**Benzoic Acid:** Two grams of N-bromoperfluorosuccinimide and one gram of benzoic acid dissolved in 20 ml of acetonitrile and allowed to stand at room temperature in the dark for 26 days lost only 4.4% of its active bromine content.
Since acetonitrile and the bromoimide showed this same percentage loss of activity in the same period of time, this would seem to indicate that benzoic acid does not react with N-bromoperfluorosuccinimide under these conditions.

**Benzaldehyde:** Two grams of N-bromoperfluorosuccinimide and one gram of benzaldehyde dissolved in 20 ml of acetonitrile and kept at room temperature for 26 days in the dark lost 23% of its active bromine content. It is presumed, although not proved, that the reaction involved here is the oxidation of benzaldehyde to benzoic acid. Nuclear bromination of benzaldehyde cannot be accomplished directly, since the product always obtained from such attempts is benzoic acid. Moreover, the experiment previously described on the reaction of N-bromosuccinimide with an excess of benzaldehyde gave a good yield of benzoic acid as the only isolated product.

7. **Reaction with Aliphatic Alcohols**

**Oxidation of Ethanol:** N-bromoperfluorosuccinimide (10.0 grams, 0.04 mole) was added to 20 ml of absolute alcohol at room temperature and the mixture was allowed to stand overnight. Subsequent working up of the product mixture resulted in the identification of the following products: \( \text{NH}_4\text{Br}, \) ethyl acetate, diethyl perfluorosuccinate, and a material giving a 2,4-dinitrophenylhydrazone which was recrystallized from aqueous alcohol to give a yellow solid
melting over a range up to 130°. This was not the 2,4-dinitrophenylhydrazone of acetaldehyde and was not further characterized. It is probable that the bromoimide, after oxidizing ethanol to acetic acid through acetaldehyde (and probably forming bromoacetaldehyde), was alcoholized to diethyl perfluorosuccinate and liberated ammonia in the process. HBr, formed by the oxidation step, reacted with the ammonia to give ammonium bromide. The acetic acid then was esterified by the excess of ethanol.

Oxidation of Cyclohexanol: N-bromoperfluorosuccinimide (2.5 grams, 0.01 mole) was added to 20 ml of cyclohexanol at room temperature. The bromoimide dissolved readily and there was a slight heating effect accompanied by the appearance of a brown color which rapidly disappeared. The reaction was complete within two minutes, since at the end of this time treatment of a small portion of the solution with aqueous KI liberated no iodine color. This solution was then reacted with a solution of 2,4-dinitrophenylhydrazine prepared according to the method of Shriner and Fuson(25) to give, after recrystallization from an alcohol-ethyl acetate-acetone mixture, 0.7 grams of a red solid, m.p. 232.0 to 232.5° (with decomposition). This was not the 2,4-dinitrophenylhydrazone of cyclohexanone. Sodium fusion gave no definite test for bromide ion. The product was not further characterized.

Oxidation of n-Propanol; To 20 ml of n-propanol (commercial
99%) at room temperature was added 2.5 grams (0.095 mole) of 95% pure N-bromoperfluorosuccinimide. Only a slight heating effect was noted and the solution produced a tan-brown color. After an hour the solution still had not de-colorized, so it was warmed on the hot plate until it became colorless. The 2,4-dinitrophenylhydrazone was formed as before to give, after recrystallization, 0.3 grams of an orange powder whose melting point was indefinite but above 250° and with decomposition. This was not the 2,4-dinitrophenylhydrazone of propionaldehyde, and it was not further characterized.

Oxidation of Isopropyl Alcohol: To 20 ml of isopropyl alcohol (commercial 99%) was added 2.5 grams (0.095 mole) of 95% pure N-bromoperfluorosuccinimide. The solution became warm and a transient brown color disappeared within two minutes, at which time the reaction was completed. The 2,4-dinitrophenylhydrazone was formed as described before. The crude derivative was recrystallized from ethyl acetate-alcohol-acetone solution to give 1.2 grams of a yellow powder of indefinite melting point which was not the 2,4-dinitrophenylhydrazone of acetone.

This reaction was repeated as follows: to three ml of isopropyl alcohol was added one gram of N-bromoperfluorosuccinimide. Reaction was complete within two minutes. To this solution was added a cold solution of semicarbazide hydrochloride neutralized with sodium bicarbonate. On
cooling the solution in an ice bath and scratching the sides of the test tube with a glass rod a white solid precipitated. This was filtered off and recrystallized from water to which a little ethyl alcohol had been added to give the semicarbazone of bromoacetone, m.p. 133 to 134°. Thus the bromoimide not only oxidized isopropyl alcohol to acetone, but it also brominated the acetone.

Subsequent qualitative tests have shown that acetone itself is readily brominated by N-bromoperfluorosuccinimide. This reaction has a short induction period after which the reaction quickly proceeds to completion. If, however, the acetone is acidified with a mineral acid such as HBr or H$_2$SO$_4$ the reaction is almost instantaneous. This indicates that the bromination occurs through the enol form of acetone.

8. Reaction with Cyclohexene: N-bromoperfluorosuccinimide (25.0 grams, 0.10 mole) of 99.6% purity was added to 200 ml of cyclohexane (as dispersing agent and diluent) in a glass flask fitted with stirrer, dropping funnel, and thermometer and cooled to 20° with a water bath. The bromoimide is not very soluble in cyclohexane. To this dispersion was added cyclohexene (16.4 grams, 0.20 mole or a 100% excess, an Eastman Kodak White Label product, peroxide number 0.026). This addition was made dropwise over a period of one-half hour in order to maintain the temperature between 21 and 24°, since the reaction was strongly exothermic. At the end of this time an iodimetric titration of an aliquot showed that
the reaction was 100% complete. The solution was water white. It was then distilled under reduced pressure from a Claisen flask to give the following cuts:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Point</th>
<th>Pressure in mm.</th>
<th>nD0.5</th>
<th>Amount</th>
<th>Identity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>up to 110°</td>
<td>3</td>
<td>solid</td>
<td>0.5 g.</td>
<td>perfluorosuccinimide</td>
</tr>
<tr>
<td>2</td>
<td>110-125°</td>
<td>3</td>
<td>1.4613</td>
<td>22.7 g.</td>
<td>adduct</td>
</tr>
<tr>
<td>3</td>
<td>125° up</td>
<td>3</td>
<td>1.4669</td>
<td>3.8 g.</td>
<td>adduct</td>
</tr>
<tr>
<td>4</td>
<td>charred residue</td>
<td>-</td>
<td>------</td>
<td>3.3 g.</td>
<td></td>
</tr>
</tbody>
</table>

Cut 1 was identified as crude perfluorosuccinimide; cut 2 was a clear liquid which had a pale blue tint, d_4^20° 1.5779, MR 57.78, ARF 1.62 and contained 24.91% bromine (theoretical for the addition product is 24.06% bromine); cut 3 analyzed for 25.99% bromine and was a clear liquid with an olive tint. Since the various possible products other than the adduct have widely different bromine contents (3-bromocyclohexene 50%, dibromocyclohexane 66%, and N-(2,3-dibromocyclohexyl)perfluorosuccinimide 39% bromine respectively), then it may be concluded that both cuts 2 and 3 consist of relatively pure adduct, N-(2-bromocyclohexyl)perfluorosuccinimide, whose structure is probably as follows:

\[
\begin{align*}
\text{(CH}_2\text{CHCHCH}_2\text{CHNCO-CF}_2
\end{align*}
\]

It may be concluded, therefore, that in this experiment N-bromoperfluorosuccinimide reacted with cyclohexene
at room temperature to give 26.5 grams (0.080 mole, 80% theoretical) of the addition product. No other product was found.

9. Miscellaneous Reactions with Inorganic Reagents: N-bromoperfluorosuccinimide is very soluble in water, and it forms a strongly acidic and oxidative solution which is water white. This solution does not precipitate AgBr when added to aqueous AgNO₃ but quickly gives a precipitate of AgBr when treated with aqueous AgNO₃. When N-bromoperfluorosuccinimide is added to an alcoholic solution of AgNO₃ a precipitate of AgBr quickly occurs.

N-bromoperfluorosuccinimide reacts instantly with aqueous KI to liberate free iodine quantitatively. It reacts with aqueous KBr also to liberate a quantitative amount of bromine. When it is dissolved in aqueous NaCl solution a deep red-brown color rapidly appears (although not instantly). This latter reaction was investigated more thoroughly as follows:

To 0.6 grams of NaCl (0.01 mole of C.P. grade) dissolved in 20 ml of water was added N-bromoperfluorosuccinimide (2.5 grams, 0.01 mole). A bromine color quickly appeared and deepened to a dark red. This solution was distilled from a 50 ml Claisen flask the side arm of which was packed with glass helices. The distillate, which obviously contained much halogen, was collected by bubbling it through 100 ml of a mixture of ice and water which
contained 4% by weight of KI. This solution turned a very deep brown and iodine precipitated. When the pot solution had turned colorless the distillation was stopped. The distillate was acidified with 10 ml of 50% $\text{H}_2\text{SO}_4$ and heated to boiling, after which it was treated with 200 ml of 2% aqueous solution (4 grams) of $\text{KMnO}_4$ added in small portions. At the end of this addition the purple color of permanganate persisted. The solution was boiled for 20 minutes to steam distill off the iodine and bromine (under these conditions chloride is not appreciably oxidized). The excess of permanganate was then destroyed by adding a few ml of ethanol. The resulting mixture, after being allowed to settle, was decanted to give a colorless decantate. Acidification of 5 ml of this solution with conc. $\text{HNO}_3$ followed by addition of aqueous $\text{AgNO}_3$ gave a voluminous curdy white precipitate of AgCl. This precipitate was collected by centrifuging and decanting. It was then agitated with 5 ml of silver-ammonia reagent (1.7 grams of $\text{AgNO}_3$ and 30 ml of conc. ammonia dissolved in 1000 ml of water. This reagent was designed specifically to preferentially dissolve AgCl in the presence of AgBr without dissolving any appreciable amount of AgBr.) (26) The mixture was centrifuged and the supernatant liquid was acidified with conc. $\text{HNO}_3$. A voluminous precipitate of white, curdy AgCl was produced. This second test confirmed the first test which indicated the presence of much chloride ion in the treated
distillate and consequently much of a volatile chlorine compound in the original reaction mixture. The method used cannot distinguish between chlorine present as Cl₂ or as BrCl; however this information is immaterial to the experiment since BrCl decomposes readily at room temperature to liberate Br₂ and Cl₂.

This experiment therefore has demonstrated that N-bromo-perfluorosuccinimide reacts with aqueous NaCl to produce either BrCl or a mixture of Br₂ and Cl₂. The reaction probably occurs as follows:

\[
\text{CF}_2\text{-CO} \xrightarrow{H_2O} \text{N-Br} + \text{NaCl} \xrightarrow{H_2O} \text{CF}_2\text{-CO-NH}_2 + \text{BrCl}
\]

then, perhaps \[\text{BrCl} \rightarrow \frac{1}{2} \text{Br}_2 + \frac{1}{2} \text{Cl}_2\]

Experiments parallel to those presented before but with the unfluorinated bromoimide (N-bromosuccinimide) show that it, too, does not precipitate AgBr when treated with aqueous AgNO₃. It slowly liberates a quantitative amount of iodine in KI solution, liberates bromine from aqueous KBr, and reacts slowly with aqueous NaCl. These reactions proceed much more rapidly in acid solution, but they are still not as rapid as those of N-bromoperfluorosuccinimide. N-bromosuccinimide does not react perceptibly with solid NaCl dispersed in dry acetonitrile. These results all tend to confirm the observation that N-bromosuccinimide, which ordinarily reacts to furnish atomic bromine,
can be caused to furnish positive bromine by the use of acid catalysts in the Lewis sense or by the use of hydroxyl solvents (2,27).

When N-bromoperfluorosuccinimide is dissolved in dry acetonitrile (Eastman Kodak White Label distilled from anhydrous CaSO₄ and stored over Na₂SO₄) to which solid granular NaCl (reagent grade) had been added, a deep red-brown color quickly developed at and around the surface of the solid NaCl. Previous experiment had shown that NaCl is inappreciably soluble in acetonitrile (supernatant liquid gave no precipitate with AgNO₃). It is presumed that the bromine coloration was caused by the formation of BrCl (which might have decomposed further into Br₂ and Cl₂).

Thus, whereas the two bromoimidazoles react similarly in aqueous solution to indicate that in both cases the bromine is present in an oxidized state, when one shifts to a non-aqueous solvent such as acetonitrile, the unfluorinated bromoimide loses its ability to react as an oxidizing agent with NaCl. Acetonitrile, being a basic solvent and thus functioning as an electron donor, might reasonably be expected to reduce the drain of electrons from the nitrogen to bromine bond and thus to decrease the positive character of the bromine atom. One would expect this effect to occur through satisfaction of the inductive fields by the solvent in the solvated state of the molecule. The fact that N-bromoperfluorosuccinimide still functions as an oxidizing
agent in acetonitrile is interpreted to mean that the nitrogen to bromine bond in this bromoimide is much more highly ionic than the one in the unfluorinated N-bromosuccinimide.

N-bromoperfluorosuccinimide, a white crystalline solid, gradually decomposes in daylight at room temperature. A sealed ampule containing this material (99.6% pure) was allowed to stand for several hours in the light at room temperature. The solid became tinted with brown, and bromine vapor appeared above it. After being allowed to stand for several days at \(-15^\circ\) in the dark, the solid again became colorless. Iodimetric analysis before and after this test showed that the sample had not lost any of its active bromine content. The same phenomenon was observed on melting a sample of the compound. It melted to give a straw-brown colored liquid which resolidified to give a light brown solid that became gradually colorless on standing at \(-15^\circ\) in the dark. The analysis again had not changed at the end of these transformations. These observations are interpreted to mean that N-bromoperfluorosuccinimide, under the influence of light and heat, undergoes some sort of equilibrium reaction which produces bromine as one of the products. The exact nature of this reaction was not determined. Solutions of N-bromoperfluorosuccinimide in ether, ethyl acetate, acetonitrile, and trifluoroacetic acid also gradually decompose to liberate a bromine color when exposed to the light.
D. Kinetic Study of the Bromination of Toluene with N-bromo-
perfluorosuccinimide

1. Reagents and Equipment: It was previously shown (pages
30 and 32) that N-bromoperfluorosuccinimide reacts with an
excess of toluene at 90° to cause bromination both in the
ring and in the side chain, whereas at 24° it reacts to
give ring bromination exclusively. A kinetic study of
the nuclear bromination was undertaken as follows.

Acetonitrile was chosen as a suitably inert solvent for
the reaction, while trifluoroacetic acid was ruled out be-
cause of its strongly acidic nature. The Acetonitrile
(Eastman Kodak White Label) was distilled from anhydrous
CaSO₄ and stored over Na₂SO₄. The toluene was C.P. grade.
The N-bromoperfluorosuccinimide was 99.56% pure by iodi-
metric titration. Sodium thiosulfate (0.1018 normal) was
used for the analyses and was standardized with sublimed
reagent grade iodine. A 4% aqueous solution of reagent
grade KI and an aqueous solution of soluble starch (as indi-
cator) were used for the titrations.

A water filled constant temperature bath, efficiently
stirred by an electrically powered stirrer and heated by
means of an electric heating element controlled by a toluene-
mercury thermoregulator, was used for the study. No cooling
system was required for the bath. This bath was adjusted
to 25.0 ± 0.1°.
2. **Experimental Procedure:** The experimental procedure is outlined as follows: stock solutions of accurately determined molarity were prepared of both N-bromoperfluorosuccinimide and toluene by weighing each compound in a calibrated volumetric flask and diluting to the mark at 25° with dry acetonitrile. Then a sample of the stock toluene solution was removed with a calibrated volumetric pipette and delivered into a two ounce brown prescription bottle the cap of which was lined with aluminum foil. An appropriate amount of dry acetonitrile, delivered from a volumetric pipette, was then added so that after addition of the stock bromoimide solution the total volume of the solution would be 50.00 ml ±0.05 ml. Then the bottle was immersed in the constant temperature bath and allowed to equilibrate to a temperature of 25.0°. At time zero an appropriate volume of accurately known molarity of the bromoimide (which had been allowed to equilibrate to 25.0°) was delivered into the reaction bottle. The reaction solution was then quickly shaken to form a homogeneous solution and a one ml sample quickly removed by means of a volumetric pipette. This sample was delivered into 25 ml of 4% aqueous KI, and the resulting mixture was titrated with standard sodium thiosulfate to a starch endpoint. The progress of the reaction was followed by removing one ml samples at successive time intervals and titrating these samples in the same manner as before. In this way a number of reactions involving various
concentrations of both the bromoimide and the toluene were carried out. These reactions were allowed to proceed to better than 25% completion.

The composition of the various reaction solutions in acetonitrile are given below:

a. 0.0707 molar bromoimide, 0.1000 molar toluene
b. 0.1414 molar bromoimide, 0.1000 molar toluene
c. 0.2121 molar bromoimide, 0.1000 molar toluene
d. 0.1414 molar bromoimide, 0.0500 molar toluene
e. 0.1414 molar bromoimide, 0.1501 molar toluene
f. 0.0504 molar bromoimide, 0.1012 molar toluene
g. 0.1008 molar bromoimide, 0.1012 molar toluene
h. 0.1512 molar bromoimide, 0.1012 molar toluene
i. 0.1008 molar bromoimide, 0.0506 molar toluene
j. 0.1008 molar bromoimide, 0.1518 molar toluene
k. control - 0.5061 molar bromoimide, no toluene

3. Treatment of the Experimental Data: The actual kinetic data are presented in Table II. This table shows that the control sample, containing only a 0.5 molar solution of N-bromoperfluorosuccinimide in acetonitrile, did not change its titration throughout the experiment. This is quantitative proof that acetonitrile is unaffected by the bromoimide under the conditions used and that acetonitrile, therefore, is a suitably inert solvent for this kinetic study.

The method of initial slopes was used for determining the reaction order with respect to both the bromoimide and
**TABLE II**

**Bromination of Toluene with N-Bromoperfluorosuccinimide in Acetonitrile at 25.0°**

<table>
<thead>
<tr>
<th>Time (Seconds)</th>
<th>Concentration in molarity of N-bromoperfluorosuccinimide remaining in the reaction solution at time t for the various reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>0</td>
<td>0.0707</td>
</tr>
<tr>
<td>1800</td>
<td>-</td>
</tr>
<tr>
<td>3600</td>
<td>-</td>
</tr>
<tr>
<td>5400</td>
<td>0.0611</td>
</tr>
<tr>
<td>7200</td>
<td>0.0631</td>
</tr>
<tr>
<td>9000</td>
<td>-</td>
</tr>
<tr>
<td>10,800</td>
<td>0.0621</td>
</tr>
<tr>
<td>14,400</td>
<td>0.0611</td>
</tr>
<tr>
<td>18,000</td>
<td>0.0606</td>
</tr>
<tr>
<td>21,600</td>
<td>-</td>
</tr>
<tr>
<td>25,200</td>
<td>0.0601</td>
</tr>
<tr>
<td>32,400</td>
<td>0.0580</td>
</tr>
<tr>
<td>46,800</td>
<td>0.0550</td>
</tr>
<tr>
<td>64,800</td>
<td>-</td>
</tr>
<tr>
<td>68,400</td>
<td>0.0509</td>
</tr>
<tr>
<td>86,400</td>
<td>-</td>
</tr>
<tr>
<td>122,400</td>
<td>-</td>
</tr>
<tr>
<td>183,600</td>
<td>-</td>
</tr>
</tbody>
</table>
the toluene. The data were used to plot the variation of concentration of the bromoimide with time at the differing initial concentrations of reactants. A representative concentration versus time plot is given in Figure I.

The general rate expression for a reaction between two substances is the following:

\[-\frac{dc}{dt} = kc_1^m c_2^n\]

Taking logarithms of both sides, the expression becomes

\[\log(-\frac{dc}{dt}) = \log k + m \log c_1 + n \log c_2\]

where \(k\) is the specific rate constant and \(m\) and \(n\) are the reaction orders of reactants \(c_1\) and \(c_2\) respectively. If a series of reactions are carried out in which \(c_1\) varies while \(c_2\) is the same in all cases, then a plot of \(\log(-\frac{dc}{dt})\) against \(\log c_1\) will give a straight line the slope of which is the order of the reaction with respect to \(c_1\). Similarly the order of the reaction with respect to \(c_2\) can be determined. The slope of the concentration vs. time curve is the overall rate of the reaction. Since reaction conditions are known accurately only at the beginning of a reaction, then the initial rate, or slope, is the one most likely to be an accurate portrayal of the true reaction between isolated molecules of the reactants. The initial slopes of the various reactions are shown in Table III.

Figure II was constructed from the initial slopes and initial bromoimide concentrations for reactions a, b, c, f, g, and h. The points lie approximately along a straight line.
REPRESENTATIVE REACTION OF N-BROMOPERFLUOROSUCCINIMIDE WITH TOLUENE IN ACETONITRILE AT 25.0° ± 0.1°

\[ R_0 = 7.50 \times 10^{-5} \text{ moles}^{-1} \text{ seconds}^{-1} \left( \frac{d[O]}{dt} = R_0 C_0^2 \right) \]

(0.101 MOLAR N-BROMOPERFLUOROSUCCINIMIDE)
(0.101 MOLAR TOLUENE)
# TABLE III

Initial Specific Rates for the Bromination of Toluene with N-bromoperfluorosuccinimide in Acetonitrile at 25.0°

<table>
<thead>
<tr>
<th>Experiment</th>
<th>c\textsubscript{1} bromoimide molarity</th>
<th>c\textsubscript{2} toluene molarity</th>
<th>initial slope x10^7</th>
<th>k\textsubscript{0-1} sec\textsuperscript{-1} x10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.0707</td>
<td>0.100</td>
<td>-6.86</td>
<td>9.70</td>
</tr>
<tr>
<td>b</td>
<td>0.141</td>
<td>0.100</td>
<td>-9.29</td>
<td>6.59</td>
</tr>
<tr>
<td>c</td>
<td>0.212</td>
<td>0.100</td>
<td>-13.6</td>
<td>6.42</td>
</tr>
<tr>
<td>d</td>
<td>0.141</td>
<td>0.0500</td>
<td>-5.80</td>
<td>8.23</td>
</tr>
<tr>
<td>e</td>
<td>0.141</td>
<td>0.150</td>
<td>-10.9</td>
<td>5.15</td>
</tr>
<tr>
<td>f</td>
<td>0.0504</td>
<td>0.101</td>
<td>-2.56</td>
<td>5.03</td>
</tr>
<tr>
<td>g</td>
<td>0.101</td>
<td>0.101</td>
<td>-7.65</td>
<td>7.50</td>
</tr>
<tr>
<td>h</td>
<td>0.151</td>
<td>0.101</td>
<td>-1.13</td>
<td>7.43</td>
</tr>
<tr>
<td>i</td>
<td>0.101</td>
<td>0.0506</td>
<td>-3.46</td>
<td>6.77</td>
</tr>
<tr>
<td>j</td>
<td>0.101</td>
<td>0.152</td>
<td>-9.80</td>
<td>6.36</td>
</tr>
</tbody>
</table>

average $k_0 = 6.92$
BROMINATION OF TOLUENE WITH N-BROMOPERFLUOROSUCCINIMIDE
REACTION ORDER WITH RESPECT TO N-BROMOPERFLUOROSUCCINIMIDE
(N-BROMOIMIDE AND TOLUENE IN ACETONITRILE AT 25.0°C)
BROMINATION OF TOLUENE WITH N-BROMOPERFLUOROSUCCINIMIDE
REACTION ORDER WITH RESPECT TO TOLUENE
(N-BROMOIMIDE AND TOLUENE IN ACETONITRILE AT 25.0°C)

SLOPE = ORDER = 0.98
The slope of this line, and therefore the order of the reaction with respect to N-bromoperfluorosuccinimide, is 1.0 (since the toluene concentration was constant within one percent at 0.100 molar). In a similar manner the initial slopes of reactions g, i, and j (where the bromoimide is constant at 0.101 molar) were used to construct Figure III. Here again these points closely represent a straight line the slope of which is 0.94.

If in a reaction involving two reagents both are present in the same concentrations, then the previous rate expression is reduced to

\[ \log(-dc/dt) = \log k + (m+n) \log c \]

and a plot of \( \log(-dc/dt) \) against \( \log c \) should give a straight line the slope of which is the overall order of the reaction \( m+n \).

Figure IV was drawn from the concentration versus time plot of reaction g, in which the bromoimide and toluene are both present initially in 0.101 molar concentrations. This graph shows that the reaction does not follow a straightforward kinetic law as the reaction proceeds, since a curve is obtained instead of a straight line. The graph can be interpreted as showing some process of inhibition which manifests itself to the greatest degree in the first few percent of the reaction.

The equation

\[ \log(-dc/dt) = \log k + \log c_1 + \log c_2 \]
BROMINATION OF TOLUENE WITH N-BROMOPERFLUOROSUCCINIMIDE

OVERALL REACTION ORDER

(N-BROMOIMIDE AND TOLUENE AT 25.0°)

(0.101 MOLAR SOLUTIONS)
is the rate expression for a second order reaction involving two reactants. This equation was solved for log \( k \), and thus \( k \), by substituting into it the various initial rates and concentrations. In this manner the rate constants (\( k_o \)) in Table III were computed. The values for the specific rate do not vary in any clear systematic manner, and the mean deviation from the mean value is 15%. It may therefore be said that the initial specific rate calculated for a second order reaction is approximately constant and is roughly \( 7 \times 10^{-5} \) moles\(^{-1}\)seconds\(^{-1} \).

There is another rate equation which is applicable to the reaction of two different substances if they are present at the same concentration. This expression is derived from the equation

\[
\frac{-dc}{dt} = kc^2
\]

by the process of integration from \( t = 0 \) to \( t \) to give

\[
\frac{1}{c} - \frac{1}{c_o} = kt
\]

In this case a plot of the reciprocal of the concentration is linear in the time, and the slope of the line is the specific rate constant \( k \).

Figure V was obtained from the data for reaction g, in which both the bromoimide and toluene are present in 0.101 molar concentrations; it shows that the rate constant is approximately constant at \( 7.9 \times 10^{-5} \) moles\(^{-1}\)seconds\(^{-1} \) for about the first 8% of the reaction. Then for the portion of the reaction between 8% and 38% completion the
BROMINATION OF TOLUENE WITH N-BROMOPERFLUOROSUCCINIMIDE

APPARENT VARIATION OF SPECIFIC RATE WITH REACTION TIME:

(0.101 MOLAR SOLUTIONS OF N-BROMOIMIDE AND TOLUENE IN ACETONITRILE AT 25.0°C)

\[ \text{Slope } K_1 = 7.9 \times 10^{-5} \text{ moles}^{-1} \text{ seconds}^{-1} \]

\[ \text{Slope } K_2 = 3.5 \times 10^{-5} \text{ moles}^{-1} \text{ seconds}^{-1} \]
specific rate is approximately constant at 3.3 x 10^{-5} moles^{-1}seconds^{-1}.

The above work has shown that the reaction of N-bromo-perfluorosuccinimide with toluene in acetonitrile at 25.0° is initially first order with respect to each reactant. However, some process of inhibition arises which causes the specific rate to decrease as the reaction proceeds.

This decrease in reaction rate and the deviation from the initial second order reaction can be shown graphically in the following manner. The reaction initially follows the rate expression

$$\frac{1}{c} - \frac{1}{c_0} = 7 \times 10^{-5}t$$

(where both reactants are present at the same initial concentrations) where $c_0$ is the initial concentration and $c$ is the concentration at time $t$. By solving this equation for $c$ and substituting into it the known value for $c_0$ and various values for $t$, one can construct a hypothetical concentration versus time curve which will show the course which the reaction would have taken had it followed the initial reaction kinetics. This was done for reaction $g$, and both the hypothetical reaction course and the actual reaction course are plotted in Figure VI for contrast. Here again it would seem that the two curves are nearly identical in the initial stages of the reaction, after which some change occurs to cause the actual reaction course to deviate from the hypothetical one.
Bromination of Toluene with N-Bromoperfluorosuccinimide

Comparison of an Actual Rate Curve (A) with a Hypothetical Curve (B) which follows the second order rate law

\[
\frac{1}{C} - \frac{1}{C_0} = 7 \times 10^{-5} t
\]

(0.101 Molar Bromoimide, 0.101 Molar Toluene in Acetonitrile at 25.0ºC)
As a search for possible causes of this inhibition, experiments were devised to test the effects of an excess of bromotoluene or of water which might have been absorbed by the reacting solutions from the air above the water bath. The other reaction product, perfluorosuccinimide, was not tested since it would seem more reasonable to consider it a catalyst rather than an inhibitor. Bromotoluene (mixed ortho and para isomers containing no trace of benzyl bromide) was prepared according to the method of Weygand (28) to give a product boiling at 179-181° at 745 mm. This was used to prepare a 5.00 molar stock solution of bromotoluene in acetonitrile. A stock solution of 5.00 molar water in acetonitrile was also prepared. The stock solutions of N-bromo-perfluorosuccinimide and toluene were those which had been used in experiments g, h, i, j, and k. It should be pointed out that these latter two stock solutions had been allowed to stand in stoppered brown bottles in the thermostat at 25.0° for ten days. During this time the molarity of the bromoimide solution had not changed.

With the use of the above materials the following reaction mixtures were prepared:

1. control - 0.101 molar bromoimide, 0.101 molar toluene
2. 0.101 molar bromoimide, 0.101 molar toluene, and 1.00 molar bromotoluene
3. 0.101 molar bromoimide, 0.101 molar toluene, and 1.00 molar water
These mixtures were allowed to react at 25.0° according to the method previously described, and the results appear in Table IV. They show that the presence of a 10 fold excess of bromotoluene (reaction m) has little effect on the total reaction rate (no essential difference between columns 1 and m); the presence of water, however, causes an appreciable increase in the total reaction rate.

When the initial rate constants were calculated from the initial slopes, however, they were found to be as follows:

reaction 1, \( k_0 = 4.1 \times 10^{-4} \text{ moles}^{-1}\text{seconds}^{-1} \)

reaction m, \( k_0 = 4.7 \times 10^{-4} \text{ moles}^{-1}\text{seconds}^{-1} \)

reaction n, \( k_0 = 5.2 \times 10^{-4} \text{ moles}^{-1}\text{seconds}^{-1} \)

A plot of \( \log(-\frac{dc}{dt}) \) against \( \log c \) for the three reactions did not agree with second order kinetics, since the curves, although nearly linear early in the reaction, had slopes which indicated reaction orders of four to six. This indicates that the reaction is complex. A representative plot is given in Figure VII.

It should be pointed out that the rate constants of these three reactions are larger than the originally determined value by a factor of about 6.5. In other words, during the ten days that the stock solutions had stood in the thermostat some phenomenon occurred which greatly increased the reactivity of the solutions, although the iodimetric titration of the bromoimide solution had not changed in
**TABLE IV**

Inhibition Study of the Bromination of Toluene with N-bromoperfluorosuccinimide in Acetonitrile at 25.0º

<table>
<thead>
<tr>
<th>Time in Seconds</th>
<th>Molarity of N-bromoperfluorosuccinimide for reactions 1, m, and n (page 64)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0993 0.0982 0.1002</td>
</tr>
<tr>
<td>1800</td>
<td>0.0931 0.0916 0.0926</td>
</tr>
<tr>
<td>3600</td>
<td>0.0891 0.0875 0.0881</td>
</tr>
<tr>
<td>5400</td>
<td>0.0850 0.0850 0.0850</td>
</tr>
<tr>
<td>9000</td>
<td>0.0804 0.0804 0.0779</td>
</tr>
<tr>
<td>14,400</td>
<td>0.0753 0.0753 0.0718</td>
</tr>
<tr>
<td>21,600</td>
<td>0.0702 0.0708 0.0646</td>
</tr>
<tr>
<td>36,000</td>
<td>0.0631 0.0641 0.0565</td>
</tr>
<tr>
<td>75,600</td>
<td>0.0519 0.0534 0.0443</td>
</tr>
</tbody>
</table>
Figure VII
Bromination of Toluene with N-Bromoperfluorosuccinimide. Overall Reaction Order

(10 day old 0.101 molar solutions of N-bromoimide in acetonitrile at 25.0°C)
this time. Infra red spectra taken of both the 10 day old bromoimide solution and a freshly prepared solution was of no help; the bromoimide solution was found to attack the NaCl cells to liberate bromine or BrCl (or both), and it was necessary therefore to use unmatched cells to obviate the danger of ruining a valuable pair of cells. The un­matched cells allowed solvent effects to appear in the spectrograms, which made them valueless for comparisons.

4. Interpretation of the Experimental Data: The factor which increased the reactivity of the 10 day old bromoimide solution is not known, but one can speculate as to its possible nature. It has been shown that a 10-fold excess of water causes a moderate increase in the overall rate, and traces of water might have a relatively much greater effect on the rate of the reaction than larger amounts.

It is also possible that absorption of air into the bromo­imide solution might cause the bromoimide to undergo a form of oxidation-reduction type of decomposition to give bromide and bromate which might alter the reactivity of the solution. An entirely different cause seems, however, more attractive.

N-bromoperfluorosuccinimide is capable of existing, theoretically, in two forms as follows:

\[
\begin{align*}
\text{CF}_2\text{CO} & \quad \text{N-Br} \\
\text{CF}_2\text{CO} & \quad \text{O-Br}
\end{align*}
\]

\(\text{(a)}\)

\[
\begin{align*}
\text{CF}_2\text{CO} & \quad \text{N} \\
\text{CF}_2\text{CO} & \quad \text{O-Br}
\end{align*}
\]

\(\text{(b)}\)
Although the form in which bromine is attached to oxygen might seem strange, yet this type of bond is considered to occur in solutions of silver trifluoroacetate to which bromine has been added, in which case trifluoroacetyl hypobromite is probably formed.

\[
\text{CF}_3\text{-C-O-Br}
\]

Although trifluoroacetyl hypobromite has never been isolated, yet considerable evidence for its existence in solution has been brought to light (18), which will be discussed later in Section IV. This type of bond exists also in the tertiarybutyl hypohalites. If these two forms of N-bromoperfluorosuccinimide did exist, and if a fresh solution of the material in acetonitrile consisted predominantly of one form, and if on standing this solution equilibrated to give a different ratio of the two forms, then this phenomenon could very neatly explain the changed reactivity of old acetonitrile solutions of N-bromoperfluorosuccinimide as compared with fresh solutions. It is quite likely that one of the two forms would be more reactive toward toluene than the other. If, for example, form (b) were more reactive than form (a), and if form (b) were to be present in only small concentrations initially, and if a solution of the bromoimide in acetonitrile were to equilibrate gradually to give a greater percentage of form (b), then an explanation is possible not only for the increased reactivity of old solutions of acetonitrile but also for the deviation
from a simple kinetic law as the reaction progresses.

If form (b) were present in fresh solutions to the extent of perhaps 10%, and if its rate of reaction were significantly greater than form (a), then the overall reaction would appear fast until most of form (b) had been used up, after which form (a) would react at a slower rate. This explanation fits the change in rate observed in Figure V. However, this discussion is only speculation, and no attempt has been made to verify it; it could, however, be tested experimentally.

It should be pointed out that work by Lauer and Oda (29) on the bromination of toluene with bromine in acetic acid shows that the rate constant decreases as the reaction proceeds and also decreases with decreasing initial concentrations. These authors explain this by saying that with toluene and tetrahydronaphthalene the reaction velocity increases with increasing concentration owing to association of the aliphatic parts leaving the phenyl group free to react; for o-xylene they say it decreases owing to increased association which screens off the phenyl group. Whether this explanation is correct is open to serious question. However, these results should be kept in mind, since certain similarities exist between the bromination of toluene with bromine and with N-bromoperfluorosuccinimide, to wit: although the reaction with N-bromoperfluorosuccinimide has not been shown to vary in the specific rate constant as the
Initial concentrations are changed, yet as the reaction proceeds it has been shown that the rate constant decreases. Whether the two phenomena have a common basis in fact is open to speculation.
II. **N-BROMOPERFLUOROGLUTARIMIDE**

A. **The Preparation of Perfluoroglutarimide**

Perfluoroglutaric acid was converted into perfluoroglutarimide according to the following scheme (17, 23):

\[ \begin{align*}
\text{CF}_2\text{-CO}_2\text{H} & \quad \overset{\text{EtOH, } \text{H}^+}{\longrightarrow} \quad \text{CF}_2\text{-CO}_2\text{Et} \\
\text{CF}_2\text{-CO}_2\text{H} & \quad \overset{\text{benzene}}{\longrightarrow} \quad \text{CF}_2\text{-CO}_2\text{Et} \\
\text{CF}_2\text{-CO}_2\text{Et} & \quad \overset{\text{NH}_3 \text{ in ether}}{\longrightarrow} \quad \text{CF}_2\text{-CO-NH}_2 \\
\text{CF}_2\text{-CO-NH}_2 & \quad 95\% \text{ H}_2\text{SO}_4 \quad \text{heat} \quad \text{CF}_2\text{-CO-N-H} \quad (89\% \text{ net yield})
\end{align*} \]

The yields corresponded closely to those reported (23). An attempt made to carry out the last step (cyclization) in 100\% H$_2$SO$_4$ rather than 95\% was defeated by the breakage of a flask, and the salvage operation gave only a 50\% yield.

B. **The Preparation of N-bromoperfluoroglutarimide**

1. **Method of Preparation:** Perfluoroglutarimide (22.1 grams, 0.10 mole) and silver trifluoroacetate (22.1 grams, 0.10 mole) were dissolved in 180 grams of trifluoroacetic acid in a one liter three neck flask fitted with mechanical stirrer, dropping funnel, and reflux condenser. To this solution was added dropwise at room temperature 16.0 grams (0.10 mole) of bromine. After the addition was complete (about fifteen minutes) stirring was maintained for fifteen minutes longer. Then the solution was filtered to remove the AgBr, and 180 grams more of trifluoroacetic acid was
used to wash the precipitate and flask. The solution was transferred to a one liter flask connected through a train of two ice-aqueous HCl traps and two Dry-Ice-acetone traps to a vacuum pump. The solvent was removed at room temperature and at a pressure varying down to 20 mm. to recover, after rectification, 305 grams of trifluoroacetic acid (85%). N-bromoperfluoroglutarimide (26.6 grams, 89% theoretical) remained in the flask as a faintly yellow syrup at room temperature. Iodimetric analysis showed this product to be 84% pure; it was not purified further.

In another experiment, in which ethyl acetate was used as the solvent, perfluoroglutarimide (110.5 grams, 0.50 mole) and silver trifluoroacetate (121.5 grams, 0.55 mole, which is a 10% excess) were dissolved in 445 grams of ethyl acetate (commercial, dried over Na₂SO₄) kept at 3 to 5° by means of an ice bath in the apparatus previously described. To this mixture was added bromine (80.0 grams, 0.50 mole) dropwise over a one-half hour period. AgBr precipitated quickly, and the stirring was maintained for one-half hour more. The mixture was warmed to room temperature and filtered to remove AgBr. The clear, colorless solution was distilled at 3 mm. with a vacuum pump protected by three Dry-Ice-acetone traps. When the mixture had been concentrated to a small volume it was transferred to a fractionating column packed with glass helices and distilled under
reduced pressure to give the following fractions at 18.0 to 18.5 mm.: 

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range</th>
<th>Weight in grams</th>
<th>Percent purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59-63°C</td>
<td>13.0</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>63-64°C</td>
<td>28.2</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>64-64.5°C</td>
<td>32.1</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>64.5-65°C</td>
<td>19.7</td>
<td>84</td>
</tr>
<tr>
<td>residue</td>
<td>-</td>
<td>3.0</td>
<td>62</td>
</tr>
</tbody>
</table>

Fractions 2 and 3 represent the highest state of purity which has been obtained of N-bromoperfluoroglutarimide.

The ethyl acetate (and/or possibly brominated products of ethyl acetate) proved exceedingly difficult to remove from the product. A further attempt to obtain a pure product by using trifluoroacetic acid as the solvent followed by fractionation of the product resulted in an unusual side reaction which will be discussed below.

It is probable that a purer product could be obtained by sublimation under reduced pressure of a few millimeters, but since N-bromoperfluoroglutarimide is a solid melting at about room temperature, the method would have to be revised for a lower temperature and a very low pressure.

2. An Unusual Side Reaction During the Preparation of N-bromoperfluoroglutarimide: During one of the preparations of N-bromoperfluoroglutarimide, an unusual side reaction was observed. The experimental details follow.
Perfluoroglutarimide (316 grams; 1.43 moles) and silver trifluoroacetate (332 grams, 1.50 moles, which is a 5% excess) were dissolved in 1314 grams of trifluoroacetic acid. To this solution bromine (229 grams, 1.43 moles) was added dropwise and with stirring. The temperature was kept at 30° with a water bath. The addition required one-half hour, after which stirring was continued for one-half hour more. Then the mixture was filtered to remove AgBr.

There was no trifluoroacetic acid available to wash the filter cake, so it was extracted with water to give a solution which contained, by iodimetric titration, the equivalent of 52 grams of bromoimide. This material was set aside for perfluoroglutaric acid recovery. The trifluoroacetic acid solution was distilled in a glass helices packed column at 20 mm., at night, under artificial light. When most of the solvent had been removed the pot material stopped boiling and then suddenly boiled violently over into the receiver and Dry-Ice trap. (Whether this sudden, violent boiling was caused by an exothermic reaction, or whether it was caused by a sudden clearing of the vacuum line is not known.) When the contaminated distillate was returned to the material in the pot, violent boiling occurred again and some material was spilled over. The remainder was re-refractionated at 20 mm. to give, after removal of the trifluoroacetic acid, the following fractions:
Gut 5 was a solid with a freezing point of about 75°. Small amounts of this material were recrystallized from water and also from cyclohexane to give in both cases a white solid, m.p. 103.9 to 104.1° which showed no depression when a melting point of a mixture of the two was taken. Sodium fusion showed the presence of nitrogen, bromine, and fluorine. The material's analysis gave 4.67% for nitrogen (Dumas) and (gravimetric silver precipitation) 29.21% for bromine. The theoretical nitrogen and bromine contents for \( \text{C}_4\text{F}_6\text{BrH}_2\text{NO} \) (bromohexafluorobutyramide) are 5.11% and 29.2% respectively. The product was tentatively identified as omega-bromohexafluorobutyramide, \( \text{Br-CF}_2\text{-CF}_2\text{-CF}_2\text{-CO-NH}_2 \), but the position of the bromine is assumed and not proved. Since all of the above fractions contained varying amounts of the butyramide, they all were recrystallized from water. The bromoimide remained in solution and was set aside for perfluoroglutaric acid recovery. The butyramide was insoluble in water and was collected and recrystallized from water and dried to give omega-bromoperfluorobutyramide (60.0 grams, 0.219 mols, 15.3% theoretical) m.p. 102.5-104.0° (the m.p. is 103.9 to 104.1° when further purified).
Although this decomposition, or degradation, is an interesting phenomenon, it is not pertinent to the present investigation and was not explored further; it seems to be a modification of the Simonini or Hunsdiecker degradation.

C. Reactions of N-bromoperfluoroglutarimide

1. Reaction with Toluene: To 50 ml of toluene in a 500 ml three neck flask fitted with stirrer and thermometer which dipped into the toluene was added N-bromoperfluoroglutarimide (15.0 grams, 0.042 mole of 84% pure material). The flask was protected from light by aluminum foil wrappings and was cooled to 26° with a water bath. When the bromoimide was added the temperature momentarily rose to 50° and then subsided again to the bath temperature (26°). After three hours of reaction a one ml aliquot showed that 0.00038 mole of positive bromine remained, and one hour later the titration had not changed, so it was considered complete. The reaction solution was amber colored. This solution was diluted with petroleum ether (30-60° b.p.) and extracted with four portions of water. The water extract was allowed to evaporate to dryness to give 8.2 grams of a white solid—the identity of which will be discussed later. The ether solution was then washed with dilute K₂CO₃, then with water, and dried over Na₂SO₄. This solution was distilled from a small Claisen flask to yield, after removal of the ether and excess toluene, 4.7 grams (65.5% theoretical) of brominated toluene b.p. 180-185°. There was no appreciable residue.
No odor of benzyl bromide was detected, but the product gave a slight positive test for labile bromine with alcoholic silver nitrate. Gravimetric analysis indicated labile bromine, calculated as 1.24% benzyl bromide. This is an 80/1 ring to chain ratio.

The apparent greater speed of reaction of N-bromoperfluoroglutarimide over N-bromoperfluorosuccinimide might be real, or it might be caused by the rise in temperature which occurred initially. This temperature rise might also be the cause of the slight increase of labile bromine in the product of the N-bromoperfluoroglutarimide reaction as compared with the N-bromoperfluorosuccinimide reaction. A more careful investigation of the relative speeds of these two reactions has not been made.

2. Miscellaneous Reactions with Inorganic Reagents: As in the case of N-bromoperfluorosuccinimide, N-bromoperfluoroglutarimide does not precipitate AgBr in aqueous AgNO₃ solution. However, it does precipitate AgBr from aqueous AgNO₂ and alcoholic AgNO₃. It reacts with aqueous KI to liberate iodine, with aqueous KBr to liberate bromine, and with aqueous NaCl to liberate either Br₂ or a mixture of Br₂ and Cl₂ or both. In short, N-bromoperfluoroglutarimide reacts in a manner very similar to that of N-bromoperfluorosuccinimide, and this is a contrast to the unfluorinated imides, where the succinimide is a brominating agent while the glutarimide is not.
III. N-BROMOTRIFLUOROACETAMIDE

A. Preparation of N-bromotrifluoroacetamide

1. A Method of Bromination Which Failed: Trifluoroacetamide (11.6 grams, 0.10 mole) (the preparation of which in high yield by the reaction of anhydrous ammonia on ethyl trifluoroacetate has been previously reported) (17) was mixed with bromine (16.0 grams, 0.10 mole), and to this mixture was added KOH (5.6 grams, 0.10 mole) dissolved in a minimum of water. The whole mixture was kept at 0° in an ice-salt bath. After the reaction mixture had stood a short while it was extracted with chloroform. However, the deep coloration of bromine was extracted into the chloroform layer, and this solution on evaporation to dryness yielded only trifluoroacetamide. Evidently the N-bromotrifluoroacetamide, if formed, reacted immediately with bromide to produce bromine.

2. The Silver Salt Method: The preparation of N-bromotrifluoroacetamide in ethyl acetate as the solvent is described as follows: silver trifluoroacetate (221 grams, 1.0 mole) and trifluoroacetamide (113 grams, 1.0 mole) were dissolved in 1000 ml of dry ethyl acetate (dried over Na₂SO₄) and bromine (160 grams, 1.0 mole) was added dropwise in the dark over the course of two hours. The temperature was kept at 0-2° by an ice bath. When the addition was completed, the mixture was filtered to remove precipitated AgBr. The resulting light orange solution was reduced to a small volume by distilling off the solvent under water pump vacuum.
The remaining liquid was then distilled in the dark at 1.0 to 1.5 mm. at 60-65° to give a tan solid, weight 116 grams. This solid analyzed iodimetrically for 25.6% bromine when neutral KI solution was used. However the titration rose to 34.2% bromine (82% pure) when the KI solution was acidified with dilute H₂SO₄. The apparent percent bromine by iodimetric titration in neutral KI solution seems to be roughly inversely proportional to the purity of the sample as determined by iodimetric titration in an acidified solution of KI.

The above product was redistilled at 6 mm pressure in a fractionating column packed with glass helices to give a product boiling at 68-69° weighing 112 grams (58.5% yield) which was 89% pure according to iodimetric titration.

Sublimation of this sample gave N-bromotrifluoroacetamide as a white crystalline solid analyzing for 40.0% bromine (theory is 41.7% bromine) and thus 95.9% pure.

N-bromotrifluoroacetamide has also been prepared in 70% yield in trifluoroacetic acid as solvent. The solvent was recovered in 92% yield.

It should be pointed out that when ethyl acetate is used as a solvent the trifluoroacetic acid, which is formed from silver trifluoroacetate, is made difficult to recover because of an ester interchange equilibrium which is set up between ethyl acetate, trifluoroacetic acid, ethyl trifluoroacetate, and acetic acid.
B. Reactions of N-bromotrifluoroacetamide

1. Reactions with Inorganic Reagents: The reactions of N-bromotrifluoroacetamide with inorganic reagents are qualitatively similar to those of N-bromoperfluorosuccinimide and N-bromoperfluoroglutarimide. It will react with aqueous KI to liberate iodine, with aqueous KBr to liberate bromine, and will not precipitate AgBr from aqueous AgNO₃. There is one difference, however. Whereas the bromoimides liberate iodine quantitatively from aqueous KI, N-bromotrifluoroacetamide has been shown to react incompletely with this reagent unless the solution is acidified. The explanation of this phenomenon probably lies in the fact that the product sodium perfluorosuccinimide (or more probably the sodium salt of the half amide acid) is a neutral salt, whereas in the case of N-bromotrifluoroacetamide the product sodium trifluoroacetamide would be a base. This would cause the solution in the latter reaction to become more basic as the reaction proceeds and might prevent the reaction from going to completion.

2. Reaction of N-bromotrifluoroacetamide with Cyclohexene: Cyclohexene (100 grams of material freed from peroxides by passing through a column of alumina) was cooled to -50° in a flask fitted with a mechanical stirrer. To this cold cyclohexene was added N-bromotrifluoroacetamide (40 grams, 0.21 moles). The bromoamide was incompletely soluble. The heterogeneous mixture was allowed to warm gradually to
room temperature. Because of inefficient stirring some bromoamide which had collected on the bottom began a strongly exothermic reaction which raised the temperature of the mixture to 40° before the reaction could be brought under control by cooling with a Dry-Ice-acetone bath. After one hour the reaction was complete as shown by failure of an aliquot to liberate iodine from KI. On cooling to slightly below room temperature with tap water, the solution precipitated a white solid which was collected by filtration and recrystallized from a mixture of cyclohexene and petroleum ether (B.p. 30-60°) to give 6.4 grams of white crystalline plates, m.p. 155.3-155.5°. This product could not be analyzed by the Kjeldahl method because it sublimed out of the digestion flask. Dumas nitrogen showed 4.93% nitrogen (theoretical for the adduct is 5.11% nitrogen). A private communication from Dr. Joseph Park of the University of Colorado (30) indicated that this compound has been shown to be the adduct. The combined filtrates were distilled at 3 mm. pressure in a small packed column to give, after removal of the petroleum ether and cyclohexene, a clear water white liquid, b.p. 65-90° at 3 mm., weight 18.5 grams. At the beginning of the distillation white crystals were deposited on the condenser surface. These were removed to give, after recrystallization from benzene, 1.4 grams of trifluoroacetamide, m.p. 73.0-74.0°.
An attempt to fractionate the liquid product under reduced pressure resulted in no clear cut separation. This liquid, on standing several days, continuously and slowly deposited crystals which, when filtered off and washed with petroleum ether, melted at 213.0 to 213.5°. Dumas nitrogen analysis showed this product to contain 15.7% nitrogen. The only product which could be imagined and which would have such a high nitrogen content was

![Chemical Structure]

(15.05% nitrogen)

However, the product was not identified.

The work with N-bromotrifluoroacetamide was discontinued when it was learned that the University of Colorado group (30) under the direction of Dr. Park was investigating a series of N-bromacetamides, including N-bromotrifluoroacetamide. They had investigated the reaction of N-bromotrifluoroacetamide with cyclohexene and had found that it gave three products; the adduct, 1,2-dibromocyclohexane, and 3-bromocyclohexene. The solid melting at 213.0 to 213.5° had not been found by them.
IV. TRIFLUOROACETYL HYPOHALITES

A. General Observations

When silver trifluoroacetate, dissolved in a suitably inert solvent such as acetonitrile or trifluoroacetic acid, is treated with an equal molecular amount of bromine there is a partial precipitation of AgBr, but the solution remains colored with bromine. Complete precipitation of AgBr can be accomplished only by heating the solution (in which case the Simonini or Hunsdiecker reaction probably takes place) or by adding to the solution some material capable of being brominated or oxidized, in which case AgBr is completely precipitated and the halogenated derivative and also trifluoroacetic acid can be isolated (acetanilide yields p-bromoacetanilide).

When silver trifluoroacetate is treated with a deficiency of bromine in an inert solvent AgBr is precipitated and a colorless solution results which liberates iodine from a KI solution (after the excess silver salt is precipitated as silver halide).

The above observations on the behavior of silver trifluoroacetate-bromine solutions have been observed also in the case of silver trifluoroacetate-iodine solutions in nitrobenzene by Hasseldine and Sharpe (32) at the University Chemical Laboratory, Cambridge.

B. The Iodination of Toluene

Silver trifluoroacetate (19) (55 grams, 0.25 mole)
dissolved in toluene (120 grams) was added dropwise to a
slurry of iodine (63.6 grams, 0.25 mole) in toluene (125
grams). An exothermic reaction immediately occurred along
with AgI precipitation and formation of trifluoroacetic acid.
The AgI was filtered off and the filtrate distilled to re-
move toluene and trifluoroacetic acid after which tolyl
iodide (45 grams, 0.81 mole; 84% theoretical) 20 D 1.6005
was then collected about 210°. A small amount of this pro-
duct was oxidized with chromic acid to give iodo benzolic
acid which after one crystallization from benzene melted
at 269 to 270°, correct for p-iodobenzoic acid.

C. Bromination of Toluene

A solution of bromine (58 grams, 0.36 mole) in carbon
tetrachloride was added to a solution of silver trifluoro-
acetate (80 grams, 0.36 mole) and toluene (33.1 grams, 0.36
mole) in carbon tetrachloride. Stirring and cooling were
maintained throughout the reaction. The product was worked
up as described before to give tolyl bromide (45 grams,
73% theoretical) 21 D 1.5512, b.p. 179 to 181°. A small
amount of this was converted into its Grignard derivative,
and the latter was carbonated to methylbenzoic acid; after
one crystallization from water a m.p. of 176 to 178° was
observed which denoted p-methylbenzoic acid.

D. Bromination of Beta-methylnaphthalene

Bromine (32 grams, 0.20 mole) was added in 30 minutes
to an ether solution (see Section I about ether as a solvent
in such reactions) of beta-methylnapthalene (36.5 grams, 0.20 mole) and silver trifluoroacetate (44.2 grams, 0.20 mole) with constant stirring and cooling to room temperature with a water bath. After filtration of the AgBr, the filtrate was brown and could not be bleached by a bisulfite wash. Distillation at reduced pressure gave: beta-methyl-
napthalene (4.8 grams, b.p. 116 to 120° at 16 mm); intermediate (1.5 grams, b.p. 120° to 140° at 16 mm); alpha-
bromo-beta-methylnapthalene (26.7 grams, b.p. 107 to 115° at 1.0 to 1.5 mm); higher boiling fraction (1.3 grams, b.p. 115 to 140° at 1.0 to 1.5 mm); residue (5.4 grams).

The third fraction (26.7 grams, 0.12 mole) represents a 50.5% conversion, and if fraction one is taken into account the net yield is 77.1%. A small amount of this product was converted into its Grignard derivative and carbonated; after one crystallization from benzene the reaction product melted at 126 to 127°, denoting beta-methyl-alpha-
naphthoic acid.

E. Testing of Other Acyl Hypohalites for Comparisons

1. Silver Acetate: Silver acetate was mechanically dispersed in an excess of toluene containing an equimolecular amount of iodine; even with vigorous stirring and gentle warming the reaction proceeded slowly. During the working up of the reaction mixture extensive decomposition was observed with liberation of iodine. The yield of tolyl iodide was only 47.5%, nD1 1.6000. A small amount of this product
was oxidized with chromic acid to give p-iodobenzoic acid, m.p. 268 to 269°. The low yield is not necessarily an indication of low iodinating power of the system however, since the silver acetate, being present as a solid phase, might have become coated with AgI to thus effectively remove part of the reactant from availability. However, this experiment does show that silver acetate would be a poor choice of silver salt for this type of halogenation.

2. Silver Trichloroacetate: In another experiment silver trichloroacetate was prepared by the action of trichloroacetic acid on silver oxide dispersed in ether. Evaporation of the ether gave the silver trichloroacetate as a white salt which was stoned in a brown bottle until ready for use (about two weeks). It was found that the silver trichloroacetate contained largely AgCl, so the material was discarded and another approach tried. To 150 ml of toluene in a Pérez flask fitted with stirrer and dropping funnel was added trichloroacetic acid (16.5 grams, 0.10 mole) and an excess of silver oxide. After neutralization of the acid had been accomplished the excess of silver oxide was filtered off. To this resulting solution was added a solution of iodine in toluene until the color of iodine persisted; this occurred when only half the calculated amount had been added. The silver precipitate was heavier than computed and contained considerable amounts of AgCl (qualitative test). During the distillation of
the product solution, much decomposition with iodine evolution occurred; no tolyl iodide was obtained, and a small charred iodine colored residue remained.

F. The Attempt to Brominate Ethyl n-Butyrate

When silver trifluoroacetate (44.2 grams, 0.20 mole) and ethyl n-butyrate (23.2 grams, 0.20 mole) were dissolved in trifluoroacetic acid (270 grams) and treated with bromine (32.0 grams, 0.20 mole), AgBr was only partly precipitated and the deep color of bromine persisted. The solution was therefore heated to reflux, at which temperature more AgBr was precipitated until there was no more silver ion remaining in the solution. There was still an excess of bromine present, however. The reaction was stopped and a quantitative amount of AgBr (38.2 grams, 0.20 mole) was collected. After recovery of the solvent, only ethyl n-butyrate (14 grams, 0.12 mole, 60% theoretical) b.p. 120° was isolated (some material was lost by spillage). No brominated product of any kind was detected in the reaction solution or the fractions of this when distilled; no Dry-Ice trap was employed in this experiment. These data indicate that at room temperature ethyl n-butyrate is inert to this type of bromination, whereas at elevated temperatures some devious reaction occurs which uses up all the silver salt while leaving considerable bromine in excess. The following sequence of reactions would offer a satisfactory explanation...
of the observed phenomena:

\[
\begin{align*}
CF_3CO_2Ag + Br_2 & \rightarrow CF_3CO_2Br + AgBr \\
CF_3CO_2H + CH_3CH_2CH_2CO_2Et & \rightarrow CF_3CO_2Et + CH_3CH_2CH_2CO_2H \\
CH_3CH_2CH_2CO_2H + CF_3CO_2Br & \leftrightarrow CH_3CH_2CH_2CO_2Br + CF_3CO_2H \\
CH_3CH_2CH_2CO_2Br & \rightarrow CH_3CH_2CH_2Br + CO_2 \\
CH_3CH_2CH_2Br + CF_3CO_2Ag & \rightarrow CF_3CO_2CH_2CH_2CH_3 + AgBr
\end{align*}
\]

G. The Attempt to brominate Benzotrifluoride

Benzotrifluoride (50 ml, an excess) and silver trifluoroacetate (22.1 grams, 0.10 mole) were dissolved in acetonitrile (50 ml). To this solution was added bromine (16.0 grams, 0.10 mole). Silver bromide was filtered off, washed, and dried to give 10.5 grams (55.8%). The filtrate, which was colored deeply with bromine, was allowed to stand in the dark at room temperature for 43 hours. At the end of that time 3.5 grams (19%) more of AgBr had precipitated. The solution was then treated with aqueous sodium sulfite to destroy the excess bromine, and the resulting AgBr was collected, washed and dried to give an additional 4.6 grams (24.5%) of AgBr. The total AgBr accounted for was 18.6 grams, 0.099 mole, or 99% theoretical. The filtrate was diluted with ether and the aqueous layer was saturated with NaCl, after which the organic layer was separated off, washed with saturated NaCl solution, and dried over CaCl_2. On distillation from a simple Claisen flask all the material (except a 1.8 gram black residue which caused lacrimation) distilled below 100°. Sodium fusion of a portion of the
distillate gave no evidence for the presence of halogen. Evidently there is some sort of an azeotrope formed among the three compounds present, i.e., acetonitrile, benzotrifluoride, and trifluoroacetic acid. However, a study of this azeotrope was not pursued. The small lacrimatory residue probably was formed by bromination of the acetonitrile.

It may be concluded, therefore, that benzotrifluoride is inert toward this method of bromination under the conditions used.
V. MISCELLANEOUS REACTIONS

A. Reaction of Perfluorocinimides with Water

1. Reaction of Perfluorosuccinimide with Water: A small amount of perfluorosuccinimide was dissolved in distilled water, and the resulting solution was evaporated to dryness to give a white solid. This solid was recrystallized twice from hot toluene to give white, short needles of perfluorosuccinamic acid (H₂NOCCF₂CF₂CO₂H), m.p. 139.7 to 140.1°, neutral equivalent 190 (theoretical is 189), analyzing for 7.36% nitrogen (Kjeldahl) (theoretical is 7.40% nitrogen). This same product was isolated from the aqueous extract of the bromination of toluene with N-bromoperfluorosuccinimide, since no depression of melting point was observed on mixing the two samples.

2. Reaction of Perfluoroglutarimide with Water: A small amount of perfluoroglutarimide was dissolved in distilled water and evaporated to dryness to yield a white solid. This solid was recrystallized from hot toluene to give perfluoroglutaramic acid (H₂NOCCF₂CF₂CF₂CO₂H), m.p. 126.5 to 127.0°, neutral equivalent 239 (theoretical is 239), analyzing (Kjeldahl) for 5.98% nitrogen (theoretical is 5.96%). This same product was isolated from the aqueous extract of the bromination of toluene with N-bromoperfluoroglutarimide. It was also obtained in a precipitate (up to 37° at 50 mm.) during the purification of perfluoroglutarimide; in this case it was probably formed by reaction of absorbed...
moisture with the perfluorocumerimide.

The foregoing results show clearly that moisture must be rigorously excluded from the reactions involving the perfluorocumarimides and bromoimidazoles lest the ring open. The fact that these perfluorinated imides can be titrated to a sharp and definite end point with standard alkali, or equally, the fact that these compounds dissolve in water to give strongly acidic solutions, cannot be construed definitely to mean that the imides themselves are strongly acidic. The reactive species probably are the half amides acids formed by hydrolytic opening of the rings.

The Preparation of N-methylperfluorosuccinimide

12 The Use of Diazomethane to perfluorosuccinimide (17.1 grams, 0.10 mole) dissolved in a small amount of ether was slowly added an ether solution of diazomethane (33) until a slight persistent yellow color was observed. The ether solution was evaporated to a small volume and a white solid crystallized from solution. This was recrystallized from ether to give 8.0 grams of shiny white plates, m.p. 97.0 to 97.2°, which had a high vapor tension and a heavy, sweet odor, similar to that of chloroform. Kjeldahl analysis indicated 6.54% nitrogen (theoretical for N-methylperfluorosuccinimide is 7.57% nitrogen). However, part of the material volatilized from the digestion flask before solution was effected in the concentrated H2SO4. Carbon-hydrogen analysis of this compound indicated 33.2% carbon and
4.09% hydrogen (theory for N-methylperfluorosuccinimide is 32.4% carbon and 1.62% hydrogen).

2. Cyclization of N,N'-dimethylperfluorosuccinimamide:

Added assurance that the above compound was, in fact, N-methylperfluorosuccinimide was gained by preparing the compound in a totally different way. To an aqueous solution of methylamine was added an ether solution of diethyl perfluorosuccinate. The resulting two-phase system was shaken thoroughly, and the precipitated diamide was filtered, dried, and recrystallized from a mixture of carbon tetrachloride and acetone to yield silky white needles of N,N'-dimethylperfluorosuccinimamide (HOC(CF)COONHCH3), m.p. 115-118°C containing 2.5% nitrogen (theoretical 2.60% nitrogen).

The gram of the above diamide was mixed with 0.5 grams of 95% H2O in a small sublimation apparatus. The pot was heated with an oil bath and a wafer pump vacuum of about 15 mm was applied. A white solid condensed on the cold finger, and this product was sublimed in the same apparatus, to give white crystals, m.p. 97.0-97.5°C. This product was shown to be identical with that previously prepared from diazomethane and perfluorosuccinimide, by mixed melting point.

This compound is insoluble in water initially, but on standing it gradually dissolves to give a strongly acid solution.
C. Reaction of Trifluoroacetic Acid with Cyclohexene

During the course of these investigations it was observed that when trifluoroacetic acid and cyclohexene were mixed the solution rapidly turned purple and then almost black and distillation of the mixture gave a fraction boiling about 150° which was tentatively identified as cyclohexyl trifluoroacetate. Therefore the following experiment was carried out: to trifluoroacetic acid (57 grams, 0.50 mole) placed in a flask fitted with reflux condenser, dropping funnel and an all-glass stirrer, was added dropwise cyclohexene (41 grams, 0.50 mole) (Eastman Kodak White Label, peroxide number 0.0). As the addition progressed a tan color developed into a dark brown; the addition required one-half hour during which the temperature rose only slightly. The mixture was then brought to reflux and was refluxed for 22 hours. During that time the temperature of reflux gradually rose from 54° to 104°. The solution was then distilled from a Cleisen flask at atmospheric pressure to give a 28.3 gram precipitate and 54.5 grams of cyclohexyl trifluoroacetate, b.p. 145-148°, nD\textsubscript{20} 1.4910. Titration of an aliquot of the precipitate showed that it contained 19.3 grams (0.138 mole) of trifluoroacetic acid. When this precipitate was redistilled, 7.0 grams more of cyclohexyl trifluoroacetate was obtained. The conversion, taking into account the trifluoroacetic acid determined in the precipitate, was 62.8%. The net yield was
then 86.8%. This product was then carefully fractionated in an efficient column to give pure cyclohexyl trifluoroacetate, b.p. 151.5°, nD20 1.3801, d41 1.18, MR 39.2, ARF 1.1. When this material was dissolved in petroleum ether (30-60° b.p.) and treated with anhydrous ammonia, a white solid precipitated which, when recrystallized from hot chloroform gave white plates of trifluoroacetamide, m.p. 71-73°. Concentration of the mother liquors resulted in a small high boiling fraction which was probably cyclohexanol.

It is to be considered highly probable that trifluoroacetic acid could be used as an elegant reagent for the preparation of alcohols from olefins with the production of trifluoroacetamide as a side product. Should the use of N-bromotrifluoroacetamide or of trifluoroacetamide itself ever become widespread, such a method as this should be seriously considered as a method of commercial preparation.
VI. PHYSICAL DATA OF NEW COMPOUNDS

1. N-Bromoperfluorosuccinimide - 99.56% pure, 31.82% Br (theory is 21.98% Br), m.p. 49.5-50.5°

2. Cyclohexene-N-bromoperfluorosuccinimide adduct freezes to a glass, b.p. 124° at 3 mm, 24.91% Br (theory is 24.06% Br), nD 1.4613, d° 1.578, MR 57.8, ARf 1.6

3. N-Bromoperfluoroglutarimide - 89% purity, 23.8% Br (theoretical is 26.7% Br), m.p. about room temperature

4. Omega-bromohexafluorobutyramid - m.p. 103.9-104.1°, 4.67% N, 29.2% Br (theory is 5.11% N, 29.2% Br).

5. N-Bromotrifluoroacetamide - 85.9% purity, 40.0% Br (theory is 41.7% Br)

6. Cyclohexene-N-bromotrifluoroacetamide adduct, that is, N-([2-bromocyclohexyl]trifluoroacetamide - m.p. 155.5°, 4.93% N (theory is 5.11% N)

7. Perfluorosuccinamic acid - m.p. 159.7-160.1°, neutral equivalent 19° (theory is 18.9), 7.36% N (theory is 7.40% N)

8. Perfluoroglutaramic acid - m.p. 128.6-127.0°, neutral equivalent 239 (theory is 239), 5.78% N (theory is 5.86% N)
9. N-Methylperfluorosuccinimide - m.p. 97.0-97.2\(^\circ\), 6.64\% N, 33.2\% C, and 4.09\% H (theory is 7.57\% N, 32.4\% C, and 1.62\% H)

10. N,N'-Dimethylperfluorosuccindiamide - m.p. 188.5-189.0\(^\circ\), 12.30\% N (theory is 12.96\% N)

11. Cyclohexyl Trifluoroacetate - b.p. 151.5\(^\circ\), \(n_D^{25}\) 1.3801, \(d_4^{25}\) 1.16, M.R. 39.2, A.Rp.1.1
VII. SUMMARY

N-Bromoperfluorosuccinimide

N-bromoperfluorosuccinimide was prepared in 85.6% yield and in 99.56% purity. It reacted with toluene at 24° to brominate exclusively in the ring, while at 90° it reacted to produce half as much benzyl bromide as bromotoluene. N-bromosuccinimide and Br₂ were reacted with toluene under the same conditions for comparison.

N-bromoperfluorosuccinimide didn't brominate benzotri-fluoride or benzoic acid. It oxidized benzyl alcohol, benzaldehyde, ethanol, 2-propanol, n-propanol, and cyclohexanol. It reacted with cyclohexene to give solely the adduct.

It reacted with aqueous AgNO₃; it did not react with aqueous AgNO₃, but it did with alcoholic AgNO₃. It was shown to liberate I₂ quantitatively from aqueous KI, Br₂ from aqueous KBr, and BrCl from aqueous NaCl. N-bromosuccinimide underwent the same reactions, although more slowly. N-bromoperfluorosuccinimide reacted with a dispersion of NaCl in acetonitrile, while N-bromosuccinimide did not.

A kinetic study of the bromination of toluene with N-bromoperfluorosuccinimide in acetonitrile at 25° showed that the reaction initially follows the kinetic expression

\[-dc/\text{dt} = 7 \times 10^{-5}c_1c_2\]

It was also shown that after reaction occurred to an appreciable extent it became complex. It was shown that bromotoluene has no effect on the reaction, while water does.
Moreover, aged solutions exhibited increased reactivity over that of freshly prepared solutions.

**N-Bromoperfluoroglutarimide**

*N*-bromoperfluoroglutarimide was prepared in 89% yield and 89% purity. In one case a side reaction resulted in a 15% yield of ω-bromohexafluorobutyramide along with the bromoimide. In these reactions investigated, *N*-bromoperfluoroglutarimide reacted very much like *N*-bromoperfluorosuccinimide.

**N₂-Bromotrifluoroacetamide**

*N*-bromotrifluoroacetamide was prepared in 70% yield and 96% purity. It reacted incompletely with aqueous KI except in acid solutions. It liberated Br₂ from aqueous KB₃ and did not react with aqueous AgNO₃. It reacted with cyclohexene to give the adduct and two unknown products.

**Trifluoroacetyl Hypohalites**

Trifluoroacetyl hypohalites (CF₃-CO₂X) were used to iodinate toluene in 84% yield, to brominate toluene in 75% yield, to brominate ω-methylnaphthalene to yield 60% of ω-bromo-β-methylnaphthalene; and were shown to be inert toward benzotrifluoride at room temperature. Trifluoroacetyl hypobromite was shown to be inert toward ethyl n-butyrate at room temperature.

**Miscellaneous Reactions**

Both perfluorosuccinimide and perfluoroglutarimide were shown to react with water to give the corresponding
Salt amide acid, Perfluorosuccinimide was reacted with
dimethane to give N-methylperfluorosuccinimide. This
same compound was prepared by reacting N,N-dimethylper-
fluorosuccindiamide with 95% sulfuric acid.

Trifluoroacetic acid was reacted with cyclohexene
to give an 81% yield of cyclohexyl trifluoroacetate.
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BIBLIOGRAPHY

1. Wohl, A., Ber. 52, 51 (1919)

2. Djerassi, C., Chemical Reviews 43 (2), 271 (1948)

3. Ziegler, K., Späth, A.; Schaf, E., Schumann, W., and Winkelmann, E., Am. 56, 1 (1942); ibid. p. 80


5. Busioli, N. P., Am. 556 (1942)


9. Winstein, S., J. Am. Chem. Soc. 64, 2788 (1942)

10. Schmid, E., Mulling, J., and Ascherl, G., Ber. 59B, 1280 (1926); ibid. p. 1876


13. Haire, J. J., and McCoy, L. L., Abstract of Papers, 56th Meeting ACS, 81L, March 27 - April 1, 1949

BIBLIOGRAPHY (CONT.)


20. Fairburn, Ethyl I., M.A. Thesis, Ohio State University (1948)


27. Winstein, S., Goodman, L., and Boschen, R. J. Am. Chem. Soc. 72, 2311 (1950)
29. Leuer, K., and Oda, R., Ber. 69B, 851 (1936), and ibid, p. 978
30. Private Communication from Professor Joseph Park, University of Colorado at Boulder, Colorado
32. Private Communication from Kaszeldine, F.N., University Chemical Laboratory at Cambridge, England
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