absorbed at 150° in a synthetic zeolite, a Linde 13X Molecular Sieve, is treated with chlorine, the ratio of secondary to primary chlorination rate constants [R (calculated on an H-atom basis) = k_s/k_p] is 1.1–1.9 (the conversion of hexane being 1.0 and 8.3%, respectively). Pretreatment of the sieve with chlorine lowers the R value further, even though the chlorine is desorbed before absorbing the hexane.

Conversion of hexane, %	R
0.71–1.7	0.3–0.8
11.8	1.9
52	2.2

At 150°, the homogeneous gas-phase reaction between chlorine and hexane yielded an R value of 2.7–3.7 (1–42% conversion, 0.5–9-sec contact time, and a molar ratio range of chlorine to hexane of 1–7). A small quantity of dichlorinated products was also obtained (*e.g.*, less than 1% in the product at 15% conversion of hexane), but these were not detected for the sieve reactions. Values for R of 2.8–6.0 in the homogeneous gas phase have been reported for the same or similar reactions.[1–3]

The pore size of the sieve is critical. Openings of 5 Å are too small to permit recovery of the product from the sieve. Openings of 13 Å are satisfactory. Openings of 10 Å appear to be borderline in value.

The increase in the value of R as the conversion is increased may be attributable to desorption of hexane from the sieve followed by reaction in the homogeneous phase. From desorption experiments with pure hexane, we have estimated that a maximum of 10% of the hexane in the sieve could have reacted in the vapor phase when the total conversion exceeded 15%. Under these circumstances, the molar ratio of chlorine to hexane in the vapor phase would be greater than 100:1 so that reaction would be rapid.

Reviewers raised the question as to whether secondary chlorides which were formed may have been dehydrohalogenated selectively to give the low R values. While no complete material balance was obtained, the following experimental facts make such a possibility remote. (1) In the normal sieve reactions, no alkenes were found. The only by-product detected was hexachlorobenzene in very small quantities. The overall time of the sieve reactions was 1–4 min. 1-Chlorohexane, deposited on the 13X sieve at 150°, left there for 80 min, and removed with steam at 150°, yielded a mixture of alkenes and 1-chlorohexane. (2) When 5A sieves were used under normal reaction conditions, product recovery was not possible as mentioned above. When the chlorination reaction was continued for extended periods of time over 5A sieves without the introduction of steam, a mixture of chlorohexanes was collected with an R ratio of 3.7–3.9, probably as a result of gas-phase chlorination. If selective dehydrohalogenation of secondary chlorohexanes occurred over sieves, the R value would be abnormally low. (3) If dehydrohalogenation were the cause of low R values, the R value would not be the increasing function of conversion noted in the text.

Experimental Section

Analysis.—The products of the reaction were analyzed by vapor phase chromatography using a 14-ft column containing 20% Carbowax on Gas-Chrom P (column temperature of 200°, feed block at 275°, with a thermal detector). The concentrations were estimated from the recorder peak heights. Pure materials and their mixtures were used to calibrate the vpc instrument, but only one secondary monochloride was available in pure form. Occasional confirmation of the identity of the individual components was made *via* nmr. A single peak on the chromatograph included all of the secondary monochlorohalides. Any component which was present in an amount greater than 0.5% would have been detected by the chromatograph.

Materials.—Linde 5X, 10X, and 13X Molecular Sieves (Union Carbide Corp) with 5-, 10-, and 13-Å pores respectively, were used directly as received ($^1/_{16}$-in. pellets). *n*-Hexane was Matheson Coleman and Bell Spectroquality; Cl_2 was 99.965% minimum purity with less than 3 ppm of water; HCl was 99.0% minimum purity, dried over H_2SO_4 before use; the nitrogen has less than 15 ppm of water and less than 0.002% oxygen.

Absorption and Desorption of Hexane on the Sieves.—The sieves were placed in a 30-in.-long, 25-mm-i.d. Pyrex tube and dried at 350–370° for 2 hr and under a stream of nitrogen. Mixed vapors of hexane and nitrogen were passed through the bed which was held at 150°. The absorption data were obtained gravimetrically. For desorption studies, pure nitrogen was passed through the bed containing the absorbed hexane. The effluent from the Pyrex tube was trapped at 0 and −76° in a series of traps. The absorption data were in reasonable agreement with those of Allen.[4]

Reaction of *n*-Hexane and Chlorine in the Molecular Sieves.—The same apparatus was used as for absorption studies with the additional precaution of eliminating free space before the sieve bed by the insertion of a close-fitting sealed Pyrex tube. Water was removed from 65 to 72 g of sieves at 450–480°. Hexane was deposited on the sieve at 150° by absorption from a stream of nitrogen. A mixture of chlorine and nitrogen was passed over the sieve for a predetermined length of time (experimental range of 1–4 min). The reactor was swept briefly with nitrogen, and the hydrocarbon was displaced from the sieve with water vapor mixed with enough nitrogen to prevent a negative pressure from forming. The time delay between the introduction of the various streams was less than 3 sec. When the water was introduced, the effluent from the reactor was led through wet and Dry Ice traps in series. After separating and discarding the aqueous phase, the excess chlorine in the trapped liquid was allowed to bleed into the atmosphere at 25° before analyzing the product. Essentially all of the chlorinated product was trapped at 0°. Fresh sieves were used for each experiment to avoid the problem of reaction between HCl and the sieves, which reaction was shown to occur slowly.

Homogeneous Gas-Phase Reaction of Chlorine and Hexane.—A Pyrex tube of 25-cc free volume served as the reactor. Mixed preheated streams of nitrogen, hexane, and chlorine were fed to the reactor at 150°. The off-gases were trapped and analyzed as described above.

Registry No.—Hexane, 110-54-3.

Acknowledgment.—Analyses, other than vpc, were performed by J. H. Turney, R. Coffee, and J. C. Randall. A. L. Caviness assisted with the experimental work.

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[4] J. L. Allen, "The Kinetics of Adsorption of Pure Hydrocarbons by Synthetic Zeolites," Thesis, Department of Chemistry, Clarkson College of Technology, Oct 29, 1964.

Perfluoro-*t*-butyl Alcohol and Its Esters

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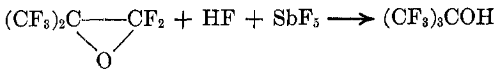
Perfluoroalkylcarbinols are especially interesting because of the large electronegativity of the fluorine atom and consequently the large inductive effects of the perfluoroalkyl group or groups.

The acidic properties of fluorine-containing alcohols and the synthesis of perfluoro-*t*-butyl alcohols have been summarized by Dyatkin, Mochalina, and Knunyants[1] and by Filler and Schure.[2] Dyatkin, *et al.*, obtained perfluoro-*t*-butyl alcohol from perfluoro-2-nitroso-2-methylpropane by oxidation to the nitrite and hydrolysis. Filler and Schure treated CCl_3Li with hexafluoroacetone. The trichloro compound was then treated with antimony pentafluoride to form the perfluoro-*t*-butyl alcohol.

$$(CF_3)_3CNO \longrightarrow (CF_3)_3CONO \longrightarrow (CF_3)_3COH$$

$$(CF_3)_2C{=}O + CCl_3Li \longrightarrow (CF_3)_2(CCl_3)COH \xrightarrow{SbF_5} (CF_3)_3COH$$

The method used in our laboratory was to use perfluoroisobutene oxide as starting material. A good yield of the alcohol is obtained and only catalytic quantities of antimony pentafluoride are required. Preparation of the oxide, the alcohol, and esters of the alcohol are described in the Experimental Section.



To obtain an estimate of the inductive effects, pseudo-first-order hydrolysis rates at pH 11 were determined for the perfluoro-*t*-butyl acetate and trifluoroacetate. These were compared with those for 1,1,1-trifluoroethyl acetate and trifluoroacetate and also those for ethyl trifluoroacetate and ethyl acetate. Table I shows the results obtained.

TABLE I

FIRST-ORDER HYDROLYSIS RATES OF FLUORO ESTERS AT CONTROLLED (CONSTANT) pH

	$t_{1/2}$, min, 5°	k, min^{-1} × 10^4 5°	15°	25°
$CH_3CH_2OOCCH_3$ (1)				24
$CH_3CH_2OOCCF_3$ (2)	<1	>6000		>6000
$CF_3CH_2OOCCH_3$ (3)	346	20	81	150
$CF_3CH_2OOCCF_3$ (4)	<1	>6000		>6000
$(CF_3)_3COOCCH_3$ (5)	23.6	294	1410	1962
$(CF_3)_3COOCCF_3$ (6)	3.2	2160		>6000

Discussion of Results

As expected, the inductive effects of the trifluoroacetate group are very pronounced under alkaline hydrolysis conditions. The trifluoromethyl group also shows an inductive effect even though it is shielded by an oxygen and a methylene group (3). The inductive effects of the *t*-butyl group (5) are over fourteen times that of the trifluoroethyl group, indicating that inductive effects are appreciably more important than steric effects. However, steric effects can be seen when **4** and **6** are compared; the perfluoro-*t*-butyl trifluoroacetate has a half-life over three times as great as the trifluoroethyl trifluoroacetate. The steric effects of the perfluoro-*t*-butyl group do extend in a measurable degree to the carbonyl group.

Acid hydrolysis of the perfluoro-*t*-butyl acetate (**5**) was found to be very slow. Thus, after 94 hr only 10% was hydrolyzed (0.1 *N* HCl in aqueous acetone). In addition to the inductive effects causing a partial positive charge at the alkyl oxygen, site of cationic attack, the steric effects of the *t*-butyl group appear to be significant.

Experimental Section

Preparation of Perfluoroisobutylene Oxide.—*Caution!* $i\text{-}C_4F_8$ is very toxic, 0.5 ppm. At 0–5° 277 g of 75% $i\text{-}C_4F_8$ (1.05 mol) was mixed with 220 ml of 30% H_2O_2, 55 ml of acetone, and 30 g of $Na_2HPO_4 \cdot 7H_2O$. While the mixture was stirring, 200 ml of H_2O containing 56 g of Na_2CO_3 was added dropwise during 85 min. Stirring was continued for 3 hr after the addition of carbonate; then the low boiling fluorocarbons were distilled out into Dry Ice cooled traps; there was 167 g of product. Ir spectroscopy showed the oxide absorption at 6.66 μ. Nmr spectroscopy indicated the oxide structure: CF_3, ϕ^* 69.6; CF_2, ϕ^* 109.2. The molecular weight utilizing a density balance was 219, theoretically 216. The boiling point of a purified fraction is 3°.

Anal. Calcd for C_4F_8O: C, 22.2; F, 70.4. Found: C, 22.1; F, 70.0.

Preparation of Perfluoro-*t*-butyl Alcohol.—To 20 g (1.0 mol) of anhydrous hydrogen fluoride and 5 g of antimony pentafluoride in a 300-ml stainless steel autoclave was charged 35 g of crude perfluoroisobutylene oxide. The mixture was agitated in an Aminco rocking mechanism at 100° for 16 hr. The product was then distilled out and passed through a steel tube (1-in. diam × 30 in. long) containing sodium fluoride pellets to remove hydrogen fluoride; 21 g of perfluoro-*t*-butyl alcohol was obtained, bp 48°. The characteristic ir absorption for the hydroxy group is at 2.74 μ. The nmr spectrum showed the tertiary alcohol structure: CF_3, ϕ^* 74.95; OH, τ 6.64.

Anal. Calcd for C_4F_9OH: C, 20.3; F, 72.15. Found: C, 20.5; F, 72.3.

Preparation of Esters.—Compounds $CF_3CH_2OOCCF_3$, $CF_3CH_2OOCCH_3$, and $CH_3CH_2OOCCF_3$ were prepared by known methods and their ir spectra compared favorably with spectra of authentic samples.

$(CF_3)_3COOCCH_3$.—To 1.90 g (0.02 mol) of 2-methylpyridine was added dropwise at 0–5° 4.72 g (0.02 mol) of perfluoro-*t*-butyl alcohol; then 4.2 g (0.02 mol) of acetic anhydride was added while stirring magnetically. Stirring was continued at room temperature for 48 hr. Distillation of the mixture gave 3.1 g, bp 81–83°, which was further purified by being passed through Drierite *in vacuo*. The ir spectrum showed the ester absorption at 5.43 μ.

Anal. Calcd for $C_6F_9H_3O_2$: C, 25.9; F, 61.5. Found: C, 26.2; F, 60.6.

$(CF_3)_3COOCCF_3$.—To 2.1 g (0.02 mol) of 2-methylpyridine cooled to 5°, 4.2 g (0.02 mol) of trifluoroacetic anhydride was added dropwise with stirring; then 4.72 g (0.02 mol) of perfluoro-*t*-butyl alcohol was added slowly. Stirring was continued at room temperature for 48 hr. Distillation of this mixture gave a main fraction, bp 57–58° (740 mm). The ir showed good material; absorption for the carbonyl was found at 5.40 μ. The material failed to give satisfactory analytical data.

Anal. Calcd for $C_6F_{12}O_2$: C, 21.9; F, 68.6. Found: C, 20.8; F, 65.6.

Hydrolysis Data.—Rates of base hydrolysis are usually determined by periodically removing samples of a reaction mixture, quenching the reaction with a known amount of acid, and back-titrating the excess acid to determine the base content of the original sample. This procedure requires a complete titration for each point on the hydrolysis curve and its accuracy is often limited because the small amount of acid formed by the hydrolysis reaction is calculated from the difference of two large quantities. The procedure used in this work is based on the maintenance of a constant pH in the reaction mixture by the controlled addition of standard base. The amount of base added at any time is then a direct measure of the acid formed by the hydrolysis reaction. Under constant pH conditions, the reaction should follow first-order kinetics and the plot of log concentration of ester *vs.* reciprocal time should be linear.

Rates of hydrolysis are obtained at constant pH by use of a Radio-meter Type TTT-1 automatic titrator controlling a motor-driven Gilmont micropipet. Reactions are carried out in 50 ml

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[1] B. L. Dyatkin, E. P. Mochalina and I. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965).

[2] R. Filler and R. M. Schure, *J. Org. Chem.*, **32**, 1217 (1967).

of 1:1 acetone–water solution contained in a 100-ml titration vessel. Before addition of the sample, the controller is set at pH 11, causing base to be delivered from the micropipet until this pH reading is reached. (In this partly nonaqueous solvent, a pH reading of 11 does not necessarily correspond to the hydroxyl ion concentration of 10^{-3}.) The amount of sample is determined from the total base requirement of the complete reaction; at pH 11 the reverse reaction should be negligible. As the acid is produced by hydrolysis of the ester, the pH of the solution tends to decrease, and the controller delivers more base from the micropipet to maintain the pH reading at 11. The buret reading at any time is a direct measure of the amount of acid produced by hydrolysis and the hydrolysis curve can be obtained by plotting buret reading *vs.* time.

First-order rate constants are obtained from the slope of the plot of log of fraction of ester remaining *vs.* reciprocal time. The ester remaining at any time is proportional to the total base required for the completed reaction minus the base already added at that time.

$$\log\left(\frac{V_{\text{total}} - V_{\text{x}}}{V_{\text{total}}}\right) = \frac{1}{kt_{\text{x}}}$$

Registry No.—Perfluoro-*t*-butyl alcohol, 2378-02-1; perfluoroisobutylene oxide, 707-13-1; $(CF_3)_3COOCCH_3$, 24165-09-1; $(CF_3)_3COOCCF_3$, 24165-10-4.

N-Bromination of Amides, Imides, and Sulfonamides with Acetyl Hypobromite

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The N-bromination of amides and imides has been accomplished by a number of workers. In most cases, successful N-bromination of amides and imides has been done by using bromine in an aqueous alkaline medium.[1] However, several investigators have devised N-brominating methods for specific compounds. Park, *et al.*,[2] used bromine with silver oxide in trifluoroacetic acid for perfluoroamides, while Neale, *et al.*,[3] used *t*-butyl hypobromite for sterically hindered amides such as N-*t*-butylpentanoamide. Also, Waugh and Waugh[4] patented a procedure to N-brominate amides which used bromine with sodium bromate in aqueous sulfuric acid.

We have discovered a new reaction in which acetyl hypobromite in carbon tetrachloride solution N-monobrominates not only imides but also unsubstituted amides, sterically hindered N-*t*-butylamides, perfluoroamides, and N-alkylsulfonamides in excellent yields. In similar fashion unsubstituted amides and sulfonamides undergo N,N-dibromination in excellent yield upon treatment with acetyl hypobromite. Numerous N,N-dibromosulfonamides have been previously prepared; however, to our knowledge N,N-dibromoamides have not yet been isolated. Examples of the N-monobromination and N,N-dibromination reaction are given using N-*t*-butyl-4-nitrobenzamide (**1**) and 4-nitrobenzamide (**2**).

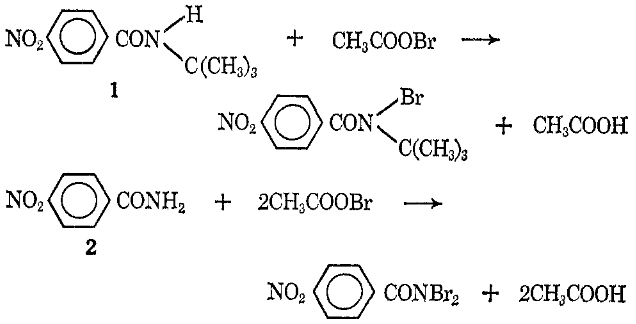
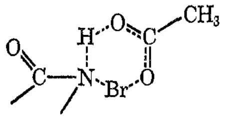


Table I gives the per cent yield of product before any recrystallization attempts were made and also gives the percentage of theoretically possible active bromine found.

The advantage of using acetyl hypobromite for N-bromination of amides and imides, in addition to the nearly quantitative yield of product obtained, is the ease with which the reactions can be carried out. A mixture of the reagent to be brominated and the carbon tetrachloride solution of acetyl hypobromite is stirred at room temperature from 15–60 min. The carbon tetrachloride solvent, the excess acetyl hypobromite, and the acetic acid by-product are evaporated at reduced pressure leaving essentially quantitative yields of very pure product. The reactions were monitored visually. N,N-Dibromo and N-alkyl-N-bromo products dissolved in the carbon tetrachloride solvent while N-bromoimides and monobromoamides settled to the bottom of the flask. Unreacted imides and amides usually floated on top of the carbon tetrachloride solvent.

A homogeneous reaction was performed using 0.0128 mmol of succinimide and 0.0140 mmol of acetyl hypobromite in 50 ml of methylene chloride. An attempt to follow the reaction by uv methods failed since the reaction was too fast. The reaction for N-bromination of amides and imides by acetyl hypobromite possibly occurs through a six-membered cyclic intermediate (or transition state).



Since the N-bromination of amides and imides with acetyl hypobromite worked so well an N-iodination of succinimide was attempted using acetyl hypoiodite. A stable solution of acetyl hypoiodite could not be prepared so the acetyl hypoiodite was prepared in an acetone solution containing succinimide which was to be iodinated. A mixture of succinimide, silver acetate, iodine, and acetone was stirred at 0° for 30 min, giving, after filtration and evaporation of the solvent, N-iodosuccinimide in 94% yield (active iodine was 98% of theory). N-Iodination of amides and imides with acetyl hypoiodite will be the topic of a future paper.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and were uncorrected. The carbon tetrachloride was distilled over calcium chloride. Bromine analyses were done by dissolving

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[2] J. D. Park, H. J. Gerjovich, W. R. Lyean, and J. R. Lacher, *J. Amer. Chem. Soc.* **74**, 2189 (1952).

[3] R. S. Neale, N. L. Marcus, and R. G. Schepers, *ibid.*, **88**, 3051 (1966).

[4] T. D. Waugh and R. C. Waugh, U. S. Patent 2,971,960 (Feb 1961).