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.

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

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**).

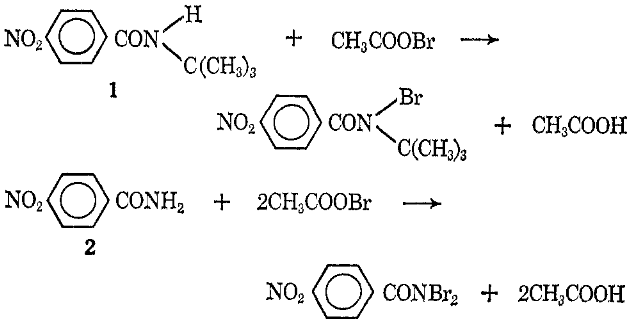
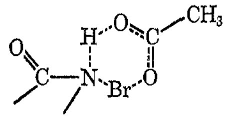


Table I gives the per cent yield of product before any recrystallization attempts were made and also gives the percentage of theoretically possible active bromine found.

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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[1] (a) F. Lengeld and J. Stieglitz, *J. Amer. Chem. Soc.*, **15**, 215 (1893). (b) F. D. Chattaway, *ibid.*, **87**, 145 (1905). (c) T. Seliwanow, *Ber.*, **26**, 423 (1893); Z. Foldi, *ibid.*, **63**, 2257 (1930). (d) H. Blitz and K. Slotta, *J. Prakt. Chem.*, **113**, 233 (1926).

[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).

TABLE I

			Mp, °C	
	Yield, %	Active bromine, % of theory	Obsd (crude)	Lit.
N-Bromo derivative of				
succinimide	98	95	168–169 dec	178 dec[a]
phthalimide	99	95	201–203 dec	206–207 dec[b]
N-methyl-4-nitrobenzamide	99	99	113–115 dec	
N-*t*-butyl-4-nitrobenzamide	99	97	131–134 dec	
4-nitrobenzamide	99	95	229–231 dec	192–202[c]
trifluoroacetamide	85	99	52–54 dec	62[d]
benzamide	98	94	126–128 dec	129–131dec[c]
N-methyl-4-toluenesulfonamide	101	98	106–107 dec	113 dec[a]
N,N-Dibromo derivative of				
4-nitrobenzamide	99	100	138–139 dec	
4-toluenesulfonamide	101	99	95–97 dec	104[a]

[a] Reference 1a. [b] Reference 4. [c] Reference b. [d] Reference 2.

the active-bromine compound in acetone, adding an equal volume of a 50:50 mixture of acetic acid and water plus an excess of potassium iodide and titrating for the released iodine with standard thiosulfate solution.

Acetyl Hypobromite.[5]—A mixture of silver acetate (5.6 g, 0.033 mol) and 150 ml of carbon tetrachloride was placed in a 500-ml round-bottom flask covered with aluminum foil. To the stirred mixture a carbon tetrachloride solution of bromine (2.15 *M*, 0.032 mol) was added dropwise over a period of 10 min as the reaction temperature was maintained at −10 ± 5°. The mixture was stirred for an additional 10 min and then filtered. The carbon tetrachloride solution was diluted to 200 ml (0.136 *M*, 0.027 mol). All other acetyl hypobromite solutions were prepared in a similar manner. Solutions of acetyl hypobromite were stable up to four weeks when stored in the dark at −10 to −15° temps. Solutions that were exposed to ordinary light at room temperature showed no activity after 8 hr. No problems were observed owing to rapid decomposition of the acetyl hypobromite.

N-Bromo-N-*t*-butyl-4-nitrobenzamide.—A mixture of N-*t*-butyl-4-nitrobenzamide (0.119 g, 0.5360 mmol) and 8 ml of acetyl hypobromite solution (0.108 *M*, 0.8061 mmol) in carbon tetrachloride was stirred at ambient temperature for 15 min in a 25-ml round-bottom flask. The flask was covered with aluminum foil to protect the product from light. The solution was evaporated at reduced pressure giving 0.1586 g of product, mp 136–137° (99% yield, active bromine was 97% of theory).

The product was recrystallized from an acetone–water mixture, giving an analytically pure material, mp 137–138° dec, ir 6.06 μ (Nujol mull) with no NH peak, uv 268 mμ (dioxane).

Anal. Calcd for $C_{11}H_{13}N_2O_3Br$: Br, 26.53. Found: Br, 26.34.

N,N-Dibromo-4-nitrobenzamide.—A mixture of 4-nitrobenzamide (0.173 g, 1.038 mmol) and 20 ml of acetyl hypobromite (0.124 M, 2.48 mmol) in carbon tetrachloride was stirred at ambient temperature for 75 min in a 50-ml round-bottom flask. The flask was covered with aluminum foil. The solution was evaporated at reduced pressure giving 0.332 g of analytically pure material, mp 138–139° dec (99% yield, active bromine was 99.7% of theory), ir 5.97 μ (Nujol mull) with no NH peak, uv 291 mμ (dioxane).

Anal. Calcd for $C_7H_4N_2O_3Br_2$: Br, 49.33. Found: Br, 49.18.

N-Bromobenzamide.—A mixture of benzamide (0.145 g, 1.20 mmol and 10 ml of acetyl hypobromite (0.126 M, 1.26 mmol) was stirred in the dark in a 25-ml round-bottom flask for 60 min at ambient temperatures. The mixture was evaporated at reduced pressure leaving 0.235 g of product, mp 126—128° dec (lit.[6] mp 129–131° dec) (98% yield, active bromine was 95% of theory).

N-Bromo-N-methyl-4-nitrobenzamide.—The N-methyl-4-nitrobenzamide was N-brominated in manner previously described in the N-*t*-butylamide. The N-bromo product was recrystallized from an acetone–water mixture, giving analytically pure material, mp 114–115° dec, ir 6.05 μ (Nujol mull) with no NH peak, uv 268 mμ (dioxane).

Anal. Calcd for $C_8H_7N_2O_3Br$: Br, 30.84. Found: Br, 30.53.

N-Iodosuccinimide.—A mixture of succinimide (0.166 g, 1.67 mmol), silver acetate (0.646 g, 3.87 mmol), and 10 ml of acetone was placed in a 50-ml round-bottom flask covered with aluminum foil. The flask was cooled in an ice bath and a solution of iodine (0.468 g, 1.84 mmol) in 15 ml of acetone was dropped in over a 5-min period. Stirring was continued for an additional 10 min. The mixture was filtered; the acetone solution was evaporated leaving 0.353 g (94% yield, active iodine was 96% of theory) of material, mp 191–193° dec (lit.[7] mp 201° dec).

Registry No.—Acetyl hypobromite, 4254-22-2; N-bromo-N-*t*-butyl-4-nitrobenzamide, 24472-09-1; N,N-dibromo-4-nitrobenzamide, 24472-10-4; N-bromo-N-methyl-4-nitrobenzamide, 24472-11-5.

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[5] H. Haubenstock and C. VanderWert, *J. Org. Chem.*, **29**, 2993 (1964).

[6] C. R. Hauser and W. B. Renfrow, Jr., *J. Amer. Chem. Soc.*, **59**, 121 (1937).

[7] C. Djerassi and C. T. Lenk, *ibid.*, **75**, 3494 (1952).

A Convenient Procedure for the Methylenation of Olefins to Cyclopropanes

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The methylenation of olefins by the method of Simmons and Smith,[2] utilizing methylene diiodide and zinc–copper couple, provides a most convenient and much used entry into the cyclopropane field. However, in spite of various modifications,[3,4] the experimental procedure still requires the preparation of rather irreproducible zinc–copper reagents.

We find that a separate preparation of the zinc–copper couple is not required; a mixture of zinc dust and a cuprous halide is even more effective. This modification reduces the experimental difficulties to the level of those encountered in an ordinary Grignard reaction.

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[1] Syntex Postdoctoral Research Fellow, 1968–1969.

[2] (a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **80**, 5323 (1958); (b) **81**, 4256 (1959).

[3] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[4] R. S. Shank and H. Schechter, *ibid.*, **24**, 1825 (1959).