more polar compounds (assumed to be diformate and hydroxyformates) which upon retreatment with formic acid and column chromatography yielded another 0.2 g of (−)-*trans*-**7**. The total yield of (−)-*trans*-**8** was 2.26 g (42%). The 97% trans portion was further purified by preparative gas chromatography: $[\alpha]^{25}\mathrm{D}$ −39.0° (*c* 2.18, $CHCl_3$); nmr 1.00 and 1.06 (6, s, methyl groups at C_2), 1.58 and 1.73 (6, doublets, methyl groups at $C_{2'}$, $J = 1$ Hz), 2.0–3.0 (3, m, H at C_3 and C_4), 4.83 (1, t, H at C_1, $J = 7$ Hz), 5.15 (1, doublet of septets, H at $C_{1'}$, $J = 10, 1$ Hz), and 7.91 ppm (1, s, formyl H); high resolution mass spectrum *m/e* calcd for $C_{11}H_{18}O_2$ 182.1306; *m/e* found 182.1256.

(+)-*trans*-2,2-Dimethyl-3-(2′-methylpropenyl)cyclobutanol [(+)-*trans*-1]. A solution of 2.00 g of (−)-*trans*-**7** (11 mmol) in 10 ml of anhydrous ether was added dropwise over a period of 20 min to a magnetically stirred slurry of 0.346 g (36.5 mequiv) of lithium aluminum hydride in 15 ml of anhydrous ether under a nitrogen atmosphere. The resulting mixture was stirred for 2 hr, an additional 30 ml of ether added, and lithium and aluminum salts were precipitated by the dropwise addition of a saturated ammonium chloride solution. The ether was decanted, and the residue washed with another 30 ml of ether. The combined ether fractions were washed in succession with dilute hydrochloric acid, saturated sodium bicarbonate solution, and brine before the solution was dried over 3A molecular sieves. Solvent was removed on the rotary evaporator giving 1.46 g of a colorless oil (86%): $[\alpha]^{25}\mathrm{D}$ +6.73° (*c* 4.47, $CHCl_3$); nmr 0.88 and 1.04 (6, s, methyl groups at C_2), 1.53 and 1.69 (6, d, methyl groups at $C_{2'}$, $J = 1.5$ Hz), 3.26 (1, s, hydroxyl group), 3.82 (1, t, H at C_1, $J = 7$ Hz), and 4.99 ppm (1, doublet of septets, H at $C_{1'}$, $J = 11, 1.5$ Hz).[7]

Acknowledgment. The authors wish to thank Professor Robert M. Coates for a preprint of his work and copies of spectra prior to publication. We also thank Dr. Roy Teranishi and Dr. Bill Haddon at Western Regional Laboratory for providing high resolution mass spectra.

Registry No.—(+)-*trans*-**1**, 52305-33-6; (−)-**2**, 7785-26-4; (−)-*cis*-**3**, 52305-34-7; (−)-*cis*-**4**, 52305-35-8; (+)-*trans*-**4**, 52305-36-9; (+)-*trans*-**5**, 52259-48-0; (+)-*trans*-**6**, 52259-49-1; (−)-*trans*-**7**, 52259-50-4.

References and Notes

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the National Institutes of Health, GM-19557, for support of this research.

(2) (a) H. C. Rilling, C. D. Poulter, W. W. Epstein, and B. R. Larsen, *J. Amer. Chem. Soc.*, **93**, 1783 (1971); (b) L. J. Altman, R. C. Kowerski, and H. C. Rilling, *ibid.*, **93**, 1782 (1971); (c) E. E. van Tamelen and M. A. Schwartz, *ibid.*, **93**, 1780 (1971); (d) R. M. Coates and W. H. Robinson, *ibid.*, **94**, 5920 (1972); (e) J. Edmond, G. Popjak, S. M. Wong, and V. P. Williams, *J. Biol. Chem.*, **245**, 4597 (1970); (f) C. D. Poulter, *J. Agr. Food Chem.*, **22**, 167 (1974); (g) C. D. Poulter, O. J. Muscio, and R. J. Goodfellow, *Biochemistry*, **13**, 1530 (1974); (h) C. D. Poulter, O. J. Muscio, C. J. Spillner, and R. J. Goodfellow, *J. Amer. Chem. Soc.*, **94**, 5921 (1972).

(3) Columbia Chemical Co.

(4) (a) P. Barbier and V. Grignard, *Bull. Soc. Chim. Fr.*, 548 (1910); (b) A. Fredga and J. K. Miettinen, *Acta Chem. Scand.*, **1**, 371 (1947).

(5) M. Delepine, *Bull. Soc. Chim. Fr.*, 1369 (1936).

(6) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 324, and references therein.

(7) W. H. Robinson, Ph.D. Dissertation, University of Illinois, Urbana-Champaign, 1972.

(8) Although Coates and Robinson[2d,7] have consistently reported the vinyl proton of *trans*-**1** as having an nmr chemical shift upfield from that of *cis*-**1**, we have always found the reverse. Examination of a spectrum reproduced in ref 7 confirms that the chemical shift of the olefinic proton for the minor isomer of the 40:60 mixture, reported to be *trans*-**1**, is indeed downfield from the cis isomer, as we have also found.

Isolation and Properties of Acetyl Hypobromite

John J. Reilly, David J. Duncan, Timothy P. Wunz,
and Robert A. Patsiga*

*Department of Chemistry, Indiana University of Pennsylvania,
Indiana, Pennsylvania 15701*

Received April 5, 1974

Acyl hypohalites (**1**) are relatively unstable substances which are decomposed by heat or light to form carbon dioxide, alkyl halides, and esters.[1-3] Of the various types which may exist only acetyl hypochlorite[4] and the perfluoroacyl hypofluorites[5] have been isolated in relative purity and characterized.

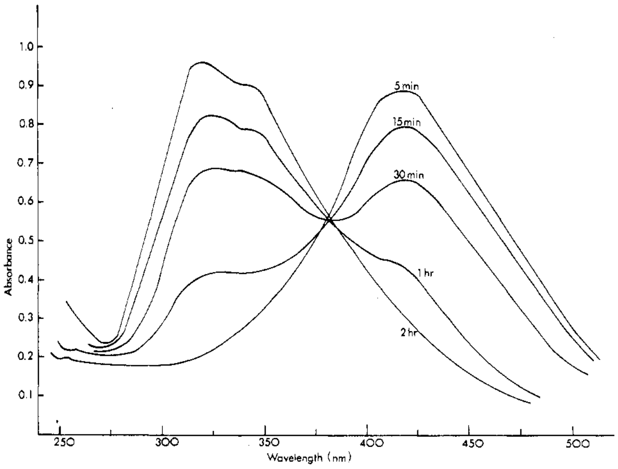
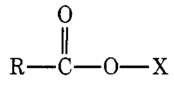


Figure 1. Absorption spectra of filtered acetyl hypobromite solutions (lines indicate extent of nitrogen purge). Initial solution: 0.05 *M* bromine and silver acetate.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-X$$

1

X = halogen

Acetyl hypobromite has been studied in solution and some properties have been reported. In carbon tetrachloride solution it absorbs in the ultraviolet region with a λ_{max} of 320 nm.[6] An infrared spectrum of the hypobromite in acetic acid shows an absorption at 670 cm^{-1} attributed to the O–Br stretching frequency by analogy with an absorption at the same frequency by *tert*-butyl hypobromite.[7] Hatanaka, Keefer, and Andrews[7] have attempted to isolate acetyl hypobromite by vacuum distillation of its solution in carbon tetrachloride, but no fraction which could be characterized as the hypobromite was detected. Beebe and Wolfe[8] found acetyl hypobromite to be stable in carbon tetrachloride at −15 to 15° for 4 weeks.

On the basis of its relatively high molecular weight and predicted polarity, acetyl hypobromite would be expected to be a high-boiling liquid or a solid. Preparation of the compound in a volatile, inert solvent which could be carefully distilled should lead to its isolation.

Results and Discussion

The reaction of bromine with silver acetate suspended in carbon tetrachloride and nitrogen flushing of any excess bromine (eq 1) yields a dark, green-yellow solution containing acetyl hypobromite. The observed color agrees with that reported by others.[7] Figure 1 shows the uv-visible spectrum of the filtered bromine-silver acetate system at various times of nitrogen purge. The quantitative aspects of the curves would be expected to vary with rate of nitrogen flow but the trends are reproducible in general form. The nitrogen flow is sufficiently slow that the stoichiometric quantity of bromine is not lost. The bromine peak at 415 nm is seen to disappear while a maximum at 320 nm persists along with a shoulder at 340 nm. A similar spectrum is obtained when perfluorinated hydrocarbon is used as solvent in place of carbon tetrachloride, the difference

$$CH_3COOAg + Br_2 \longrightarrow CH_3COOBr + AgBr \qquad (1)$$

being the primary peak shifting to 318 nm and the shoulder having a lower intensity (about 75% that in CCl_4).

Slow vacuum distillation of this filtered carbon tetrachloride solution produces a pale yellow, fluffy solid composed of tiny, needle-like crystals. Absorption maxima identical with those of the original filtered solution are shown in the uv spectrum of a solution of the crystals redissolved in CCl_4.

When the crystals are removed from cold (0°) surroundings and nitrogen atmosphere into the room they gradually take on a deliquescent appearance, turn dark red-brown or occassionally green, and gradually disappear. The change is most likely brought on by reaction with moisture in the air, since the crystals appear to remain unchanged if kept for several minutes at room temperature but under nitrogen.

Several methods for weighing the crystals as part of an equivalent weight determination were explored. The most satisfactory procedure is to weigh the crystals in water. Even though acetyl hypobromite reacts with water, no change in the number of equivalents of oxidant should occur. Four iodometric determinations were made by this method. The average is 143.5 ± 5 and the expected value is 138.9.

The molar absorptivity of acetyl hypobromite in CCl_4 with concentrations determined by titrating the filtered reaction mixture and constructing a Beer's law plot was found to be 203 ± 10. If the determination was performed by weighing the isolated solid in CCl_4, the absorptivity was found to be 192. One determination based on weighing the dry, isolated solid gave a value of 212.

The evaluation of infrared spectra of acetyl hypobromite in carbon tetrachloride has the advantage over acetic acid in that carbon–hydrogen and carbonyl absorptions can be observed.

The original filtered acetyl hypobromite solution and redissolved crystals have identical absorption features which are consistent with the structure. Carbon–hydrogen stretching and bending bands occur in the expected region for the methyl group, the carbonyl stretch appears at 1790 cm^{-1}, an absorption at 1180 cm^{-1} may be assigned to the C–C–O group by analogy with absorption by acetyl hypochlorite,[9] and a medium to weak absorption at 680 cm^{-1} is assigned to the O–Br stretch. Depending on exposure of the carbon tetrachloride solution to air and warmth during preparation of the infrared sample, absorptions characteristic of acetic acid and carbon dioxide may be seen.

The proton magnetic resonance spectrum of acetyl hypobromite in carbon tetrachloride gives a single peak at δ 2.25. This is identical with the reported absorption by acetyl hypochlorite.[9]

Experimental Section

Materials. Carbon tetrachloride was distilled at atmospheric pressure in a stream of dry nitrogen and stored over molecular sieve. Commercial silver acetate was used without purification. Bromine was distilled from P_2O_5 just prior to use. The fluorocarbon used was FC-75 (bp 102°) obtained from the 3M Co.

Spectral Procedures. Infrared liquid cells of sodium chloride or potassium bromide were used to contain the samples solutions. Ultraviolet spectra were run with pure solvent as reference. Pmr spectra showed no absorptions in the δ 10–12 region indicative of the acetic acid proton.

General Procedure. All experimental work was conducted in subdued light, using red light bulbs when necessary to see the equipment. The all-glass apparatus used to prepare the acetyl hypobromite solution was U-shaped. The larger arm (approximately 200 ml capacity) had a coarse fritted disk to permit filtration. The narrower arm provided an inlet for nitrogen and was fitted near the bottom with a Teflon stopcock and outlet tube. The aparatus was jacketed in a light-proof case with only the stopcock protruding. The inner space was packed in ice. The empty apparatus was flushed with nitrogen prior to addition of silver acetate and one-half the required amount of CCl_4 into the larger arm. The heterogeneous mixture could be kept agitated by the nitrogen gas passing through the glass disk. Bromine dissolved in the remaining portion of CCl_4 was added dropwise over 15 min, the solution constantly being agitated by a slow stream of nitrogen. The nitrogen flow was then increased and samples were taken periodically for spectrophotometric determination of bromine and hypobromite content. Typical quantities used were: silver acetate, 8.4 g (0.050 mol); bromine, 3.0 ml (0.058 mol); CCl_4, 150 ml. Samples were taken from the apparatus by reversing the direction of nitrogen flow, thus applying pressure on the surface of the solution. The solution was then forced through the filter disk and out of the stopcock. When the bromine was seen to be absent as indicated by the lack of a shoulder on the hypobromite absorption peak, the solution was considered ready for distillation of solvent. The time from combination of reactants to this point in the procedure was 2–3 hr.

The isolation of the acetyl hypobromite was accomplished by transferring the reaction solution (*via* the above-described filtration) to a distillation flask. The transfer and subsequent assembly of the distillation apparatus were done while a slow stream of nitrogen passed over the solution. The success in isolating solid acetyl hypobromite depends on vacuum distilling the CCl_4 at an extremely slow rate. Otherwise, acetyl hypobromite has a great tendency to transfer with the solvent. Moderate vacuums such as those obtained by a simple water aspirator (water vapor removed by placing a drying tower in the vacuum line) permitted the slow (2–4 hr) distillation of 75% of the solvent. This was followed by switching to a vacuum pump, maintaining 5–10 mm pressure. Intermittent opening and closing the line to the pump was found to be helpful in preventing bumping and distillation of the hypobromite. Throughout all distillations the distilling flask was packed in ice. Finally, as solid began to appear the vacuum was decreased to <5 mm, and pumping was continued until the crystals appeared very dry.

The pressure was returned to 1 atm with nitrogen to allow disassembly of the apparatus. The solid hypobromite was removed for sampling from the flask by using a glass spatula, maintaining a slight positive pressure of nitrogen and a temperature of 0°. Approximately 1 g of solid acetyl hypobromite could be isolated in a typical experiment.

Solutions for equivalent weight determinations were prepared by placing the weighed solid (~0.1 g) in a mixture composed of H_2O (5 ml), KI (2.5 g), and acetic acid (10 ml). The liberated iodine was then titrated with 0.100 *M* thiosulfate.

The fluorocarbon was poorly suited as a solvent. Bromine was only partially soluble in it, and it was not possible to obtain appreciable hypobromite, as indicated by very weak absorptions in the 320–340-nm region. Methylene chloride also proved to be unsuitable. Attempts with this solvent gave solutions with a pronounced acetic acid odor, suggesting that the hypobromite is unstable and yields acetoxy radicals which abstract hydrogens from the solvent.

A method for determining the melting point of acetyl hypobromite could not be devised.

On one occasion, when a flask containing some residue of the crystals was held in the hand, the crystals decomposed with an audible "pop" and a small puff of smoke. During another experiment approximately 50 mg of the crystals was placed on a hot plate and only minor spattering was observed. Nevertheless, as a precaution, the isolation of large quantities (>5 g) of solid acetyl hypobromite should be performed with adequate shielding.

Registry No.—Acetyl hypobromite, 4254-22-2; silver acetate, 563-63-3; bromine, 7726-95-6.

References and Notes

(1) D. D. Tanner and N. J. Bunce, "The Chemistry of Acyl Halides," S. Patai, Ed., Interscience, New York, N. Y., 1972, pp 455–500.

(2) C. V. Wilson, *Org. React.*, **9**, 332 (1957).

(3) R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956).

(4) P. Schutzenberger, *C. R. Acad. Sci.*, **52**, 135 (1861).

(5) R. L. Cauble and G. H. Cady, *J. Amer. Chem. Soc.*, **89**, 5161 (1967).

(6) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

(7) Y. Hatanaka, R. M. Keefer, and L. J. Andrews, *J. Amer. Chem. Soc.*, **87**, 4280 (1965).

(8) T. R. Beebe and J. W. Wolfe, *J. Org. Chem.*, **35**, 2056 (1970).

(9) J. C. Evans, G. Y.-S. Lo, and Y.-L. Chang, *Spectrochim. Acta*, **21**, 973 (1965).