Spectra were recorded with a Varian HR-60, Model 4300-B using a V-4331 nmr probe which was equipped with a V6040 temperature controller. To determine the temperature in the reaction mixture, an nmr tube, containing some liquid into which a thermocouple was inserted, was placed in the probe. In this way it was determined at what temperature the thermocouple in the probe had to be maintained in order to get a certain temperature in the reaction mixture. By constant monitoring of the temperature controlling device it was possible to maintain the temperature to within  $\pm 0.5^{\circ}$  of the desired temperature. The various peak areas were measured with a Keuffel and Esser planimeter which measured areas to 0.1 cm<sup>2</sup>. The times mentioned throughout the text are the times after insertion of the reaction mixture into the probe that the spectrum was scanned through the molozonide methine proton absorption.

There is a question of the solubility of the ozonolysis products, particularly the oligomer, in the reaction mixture. The total methine proton areas of the first and last spectra were about the same. The dimethyl ether solution was finally warmed to  $-50^{\circ}$ ,

and the total methine proton areas of the spectrum which was obtained at this temperature agreed well with that from the first spectrum which was recorded at  $-103^{\circ}$ . This was some indica-

tion that the oligomer was in solution. The molozonide had nmr ( $CCl_2F_2$ )  $\delta$  4.07 (t, CH), 1.60 (m, CH<sub>2</sub>), 0.90 (t, CH<sub>3</sub>); nmr ( $CD_3OCD_3$ )  $\delta$  4.28 (t, CH), 1.67 (m, CH<sub>2</sub>), 0.95 (t, CH<sub>3</sub>). Authentic ozonide had nmr (CCl<sub>4</sub>)  $\delta$ 4.94 (t, J = 5 Hz, CH), 4.89 (t, J = 5 Hz, CH), 1.55 (m, CH<sub>2</sub>), 

Registry No.-Molozonide (trans-3-hexene), 2028-40-2: trans-3-hexene, 13269-52-8.

Acknowledgment.--We are indebted to the National Science Foundation for partial financial support and to Dr. Dewald for discussions about some of the data.

## **Reaction of Hypochlorous Acid with Ketones.** A Novel Baever-Villiger Oxidation of Cyclobutanone with Hypochlorous Acid

J. A. HORTON, M. A. LAURA, S. M. KALBAG, AND R. C. PETTERSON<sup>1</sup>

Chemistry Department, Loyola University (New Orleans), New Orleans, Louisiana 70118

Received February 24, 1969

Cyclobutanone was converted into  $\gamma$ -butyrolactone by aqueous hypochlorous acid, apparently the first case of a Baeyer-Villiger reaction by a nonperoxidic oxidant. This reaction is accelerated by acid, unaffected by light, and does not involve the intermediacy of 4-chlorobutyric acid. Neither cyclopentanone nor cyclohexanone are oxidized to lactones by HOCl. Cyclohexanone gives 2- and 4-chlorocyclohexanone, 2,2-dichlorocyclohexanone, and 2-cyclohexenone, but no 3-chlorocyclohexanone.

The Baeyer–Villiger oxidation of ketones to esters has been observed with various peroxy acids, including hydrogen peroxide,<sup>2</sup> and apparently with alkyl hydroperoxides.<sup>3</sup> but has been strictly limited to oxidants containing the -OOH group.

Little is known about reactions of hypochlorous acid with ketones, and it appeared possible that this acid, which resembles peroxy acids in being both a weak acid and an oxidizing agent, might also convert ketones into esters.

We have treated a few simple ketones with aqueous hypochlorous acid at various pH's and examined the products. With cyclohexanone and cyclopentanone no trace of the appropriate lactones could be detected by glpc, the major result being chlorination. However, cyclobutanone was rapidly oxidized to  $\gamma$ -butyrolactone in 83% yield at pH 4.

Although this oxidation of cyclobutanone appears to be a rather special case, it was of interest to subject it to some mechanistic tests. The main alternative to a Baeyer-Villiger type (ionic) mechanism (Scheme I) is a radical ring opening to give 4-chlorobutyric acid (5)



<sup>(1)</sup> To whom inquiries should be addressed.



followed by a cyclization of the chloro acid 5 to the lactone (Scheme II). A third highly unlikely possibility is an unprecedented free-radical analog of the Baeyer-Villiger reaction (Scheme III). In all these mecha-



nisms we assume as the first step an addition of hypochlorous acid to the keto group to give 1 which is analogous to that accepted for peroxy acids in the Baever-Villiger reaction. Scheme II involves a radical ring opening similar to one which is well established for alkyl hypochlorites;4,5 e.g., cyclobutyl hypochlorite decomposes thermally to 4-chlorobutyraldehyde.<sup>5</sup> This mechanism was excluded by subjecting the proposed intermediate 4-chlorobutyric acid to the conditions of the

<sup>(2)</sup> C. H. Hassall, Org. Reactions, 9, 73 (1957); H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 123. (3) D. C. Dittmer, R. A. Fouty, and J. R. Potoski, Chem. Ind. (London), 152 (1964).

<sup>(4)</sup> See, for example, F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. (a), W. N. Smith, and P. M. Zanet, J. Org. Chem., 38, 55 (1963).
(5) D. B. Denney and J. W. Hanifin, Jr., *ibid.*, 29, 732 (1964).

reaction and recovering all of it by glpc as its methyl ester after treatment with diazomethane. In a parallel experiment with cyclobutanone, no methyl  $\gamma$ -chlorobutyrate was detectable by glpc.

Schemes II and III include a homolytic cleavage of the O-Cl bond in adduct 1 which should be accelerated by light. In fact, irradiation with a strong 3000-4000-Å light source had no effect on the yield of lactone. Two identical solutions of cyclobutanone in hypochlorous acid, one protected from light, were cooled in ice, irradiated for a short time, quenched with bisulfite, and analyzed for lactone by glpc. The yield of  $\gamma$ -butyrolactone was  $65 \pm 1\%$  in both cases.

If this evidence is accepted as eliminating Schemes II and III, only the Baeyer-Villiger ionic mechanism seems to remain. One further test was performed. Baeyer-Villiger reactions are catalyzed by acid,<sup>2</sup> while the only expected effect of pH on a radical reaction would be its influence upon the fraction of hypochlorous acid present at equilibrium in un-ionized form (rather than as OCl<sup>-</sup>). The rate of a radical reaction would probably be proportional to the concentration of the hypothetical adduct 1, which in turn would no doubt depend on the concentration of HOCl.

Using  $3.8 \times 10^{-8}$  as the ionization constant of hypochlorous acid<sup>6</sup> the percentage of HOCl present as such is calculated to be 100% at pH 4, 72% at pH 7, and 0.003% at pH 12. One-point rate experiments done at pH 4, 7, and 12 gave yields of  $\gamma$ -butyrolactone of 83, 30, and 27% respectively. Thus, the rate is not directly related to the concentration of HOCl and the reaction appears to be acid catalyzed.

We conclude that Scheme I best fits the facts available and that the cyclobutanone reaction is very likely the first case of a Baeyer-Villiger reaction with a nonperoxidic oxidant. From the failure of the reaction with the five- and six-membered cyclic ketones it is evident that the driving force is marginal and requires help from ring strain to compete with other reactions such as chlorination.

The reaction of cyclohexanone with hypochlorous acid at pH 4.6 was reproducible only in that  $\epsilon$ -caprolactone was never detectable. Unfortunately, the yields of the various products varied uncontrollably, defeating our plans for a detailed study. The products were: 2chlorocyclohexanone (4-16%), 4-chlorocyclohexanone (4-48%), 2,2-dichlorocyclohexanone (0-16%), 2-cyclohexenone (0-20%), and 6-chlorohexanoic acid (0.1%). Surprisingly, no 3-chlorocyclohexanone was ever detected although the 2- and 4-chloro isomers were always both found. Conceivably the 3-chloro ketone dehydrohalogenates to 2-cyclohexenone under the conditions used, but in some reactions none of the latter was found either. The disappearance of active chlorine was greatly accelerated by light, indicating that radical reactions predominate with cyclohexanone. Chlorohexanoic acid is presumed to arise by a radical mechanism of the Scheme II type, which must be extremely slow compared with chlorination.

## **Experimental Section**

Aqueous hypochlorous acid solutions were prepared by adding glacial acetic acid to Purex or Clorox household bleach until

the desired pH was indicated on a pH meter. When fresh, household bleach contains 5-6% sodium hypochlorite as well as 5-6% sodium chloride and small amounts of sodium chlorite, sodium chlorate, sodium hydroxide, and oxygen. When transferred from the original plastic containers to brown glass bottles and stored at 5° the composition remained nearly constant for many months. Ir spectra were taken on Perkin-Elmer Model 237 and 337 grating spectrometers. Except where noted glpc was done with thermal conductivity detectors, using  $210 \times 0.8$  cm i.d. glass columns packed with 60-80 mesh Chromosorb P containing 20% liquid phase.

Reaction of Cyclobutanone with Hypochlorous Acid .--- A solution of hypochlorous acid, made from 6% sodium hypochlorite (10 ml) by rapid addition of acetic acid to pH 4.0, was diluted with water to 25 ml and added to cyclobutanone (51 mg). After 15.0 min at room temperature, the remaining active chlorine was quenched with 10% aqueous sodium bisulfite and the mixture was extracted five times with ether (15 ml). The extracts were washed with saturated sodium sulfate and dried with anhydrous sodium sulfate, and most of the ether was evaporated. Alcoholfree ethereal diazomethane was added to the residue until its color persisted, and after 2 days at about  $5^{\circ}$  the colorless solution was treated with additional diazomethane for 1 hr. The more volatile components were removed by rotary evaporation (25 torr, 25°) and the residue was gas chromatographed (DC-550, The major product was  $\gamma$ -butyrolactone, identified by 115°). comparing its retention time (9 min) and infrared spectrum with those of an authentic sample. A peak with the retention time of methyl 4-chlorobutyrate appeared which was too small to collect. However using a 50-ft diethylene glycol succinate support coated capillary glpc column (Perkin-Elmer Co.) with flame detectors it was established that, if any 4-chloro acid was produced, its yield was less than 0.5%

Stability of 4-Chlorobutyric Acid.-4-Chlorobutyric acid (60 mg) was treated with hypochlorous acid under similar conditions and recovered unchanged (as the methyl ester). No  $\gamma$ -butyrolactone was formed. The free chloro acid generally cyclized quantitatively to  $\gamma$ -butyrolactone in the injection port of a gas chromatograph at temperatures as low as 100°. The methyl ester appears to be unaffected by ordinary glpc conditions.

Effect of pH.-Three 15-ml portions of 5% bleach were adjusted to pH 4, 7, and 12, made up to 25 ml, and added to 45-mg samples of cyclobutanone. After 15.0 min each was quenched with 10% sodium bisulfite and extracted continuously with The extracts were dried (sodium sulfate) and conchloroform. centrated by distillation of most of the solvent through a 6-in. Vigreux column. Glpc marker (fenchone) analysis gave the following conversions into  $\gamma$ -butyrolactone: pH 4, 83%; pH 7, 30%; pH 12, 27%.

Effect of Light.-A mixture of 5% bleach (16.5 ml), sodium acetate (1 g), acetic acid (2 ml), and cyclobutanone (147 mg) of pH 4.8 in a Pyrex tube was cooled in an ice-water bath and irradiated for 75 min with 16 8-W black light "3500A" lamps in a Rayonet photochemical chamber reactor (Southern New England Ultraviolet Co.). After a work-up like that of the pH experiments the yield of lactone was found to be 65.0%. The yield in a dark control was the same within experimental error (65.8%).

2,2-Dichlorocyclohexanone.-Cyclohexanone (10 g) was chlorinated with sulfuryl chloride (28 g) in dichloromethane by the method used by Stevens and coworkers' for the chlorination of butyraldehyde. Fractional vacuum distillation gave 4.4 g of 2,2dichlorocyclohexanone as a colorless oil:  $n^{24}D$  1.4949; ir (neat) 1745 (C=O), 1120, 990, 835, 805, and 740 cm<sup>-1</sup> (lit.<sup>8</sup> n<sup>15</sup>D 1.4969. ir (CCl<sub>4</sub>) 1744 cm<sup>-1</sup>).

4-Chlorocyclohexanone was prepared from 1,4-cyclohexanediol by a known method:<sup>9</sup> ir (CS<sub>2</sub>) 1725 (C=O), 1325, 1255, 1130, 850, and 780 cm<sup>-1</sup>. Anal. Calcd for C<sub>6</sub>H<sub>9</sub>ClO: C, 54.35; H, 6.84. Found: C, 54.51; H, 6.52.

3-Chlorocyclohexanone was prepared by a known method:<sup>10</sup> ir (CS<sub>2</sub>) 1705 (C=O), 1325, 1250, 1125, 1025, 904, and 845 cm<sup>-1</sup>.

6-Chlorohexanoic acid was synthesized both by a radical ring opening of cyclohexanone<sup>11</sup> and by acid hydrolysis of  $\epsilon$ -chloro-

<sup>(6)</sup> M. W. Lister, Can. J. Chem., 30, 879 (1952).

<sup>(7)</sup> C. L. Stevens, E. Farkas and B. Gillis, J. Amer. Chem. Soc., 76, 2695 (1954).

<sup>(8)</sup> A. Kirrman, M. Vilkas, and D.-Q.-Quan, Compt. Rend., 248, 418 (1959).

<sup>(9)</sup> R. Grewe, W. Lorenzen, and L. Vining, Ber., 87, 793 (1954).

<sup>(10)</sup> A. Kötz and T. Grethe, J. Prakt. Chem., [2] 80, 503 (1909).
(11) J. B. Braunworth and G. W. Crosby, J. Org. Chem., 27, 2064 (1962).

capronitrile: ir (CS<sub>2</sub>) 3500, 2950, 1715 (CO<sub>2</sub>H), 1275, 965, 740 cm  $^{-1}.$ 

 $\epsilon\text{-}Caprolactone,$  2-cyclohexenone, and 2-chlorocyclohexanone were commercially available.

**Glpc Retention Data.**—On a DC Hyvac silicone grease on Chromosorb P column, retention times, R, relative to 2-chlorocyclohexanone follow: cyclohexanone, 0.45; 4-chlorocyclohexanone, 1.15;  $\epsilon$ -caprolactone, 1.65; 3-chlorocyclohexanone, 1.9; 2,2-dichlorocyclohexanone, 2.0. 2-Cyclohexenone and 4-chlorocyclohexanone in our product mixtures were better separated by 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P (R 0.45 and 1.45, respectively).

Reaction of Cyclopentanone with Hypochlorous Acid.—The retention time of  $\delta$ -valerolactone was determined with a sample made by oxidizing cyclopentanone (1 g) with *m*-chloroperbenzoic acid (2.06 g) in chloroform (25 ml) for 2 days at room temperature. The ir of the lactone compared well with the published<sup>12</sup> spectrum. No indication of a peak with this retention time was observed upon glpc analysis of the products of reactions between cyclopentanone (0.1 mol) and aqueous hypochlorous acid (0.4 mol) at pH 6 which were allowed to proceed until the active chlorine disappeared. The products were not identified.

Reaction of Cyclohexanone with Hypochlorous Acid .- To 400 ml of 5.2% aqueous sodium hypochlorite (0.28 mol) was added enough glacial acetic acid to bring the pH to  $4.6 \pm 0.1$  (about 55 ml). Cyclohexanone (7.5 g, 0.076 mol) was added and the mixture was stirred at room temperature, protected from light, until a negative test for active chlorine was obtained with starch-iodide paper (20-60 hr). The mixture was extracted with chloroform and the chloroform extracts were washed with 5% sodium bicarbonate. In one experiment the bicarbonate washings were acidified and extracted with chloroform, from which a little 6chlorohexanoic acid (0.1%) was obtained as the methyl ester by evaporation, treatment with diazomethane, and glpc collection. The original chloroform extract was concentrated and analyzed by preparative glpc, usually with ethyl phenylacetate as an internal standard. All major and most of the minor products were identified by comparing their glpc retention times and ir spectra with those of authentic samples. A few experiments were run at other pH values between 2 and 7 and the products

(12) R. S. Rasmussen and R. R. Brattain, J. Amer. Chem. Soc., 71, 1073 (1949).

were examined mainly for  $\epsilon$ -caprolactone, none of which was ever detected. Several tests of the effect of irradiation with 3000-4000-Å light at various temperatures were done. The reaction vessel was cooled with ice-water in a Pyrex dewar for the runs at 2°. Reproducibility was poor, especially in the dark reactions, and the erratic material balances suggest that a variable amount of polymeric material was usually formed; this was not investigated.

Glpc analyses of "typical" runs for unchanged cyclohexanone (6), 4-chlorocyclohexanone (7), 2-chlorocyclohexanone (8), 2cyclohexenone (9), and 2,2-dichlorocyclohexanone (10) are given in Table I.

TABLE I REACTION OF CYCLOHEXANONE WITH HYPOCHLOROUS ACID AT pH 4.6

Conditions <sup>a</sup>			Conversions, <sup>b</sup> %				
	°C	Time, hr	6	7	8	9	10
Dark	25	60	18	10	8.9	0.0	0.0
Dark	25	<b>21</b>	92	1.3	3.5	0.0	4.3
Dark	30	18	53	22	6.2	9.3	Trace
3500 Å	40	0.5	15	14	3.0	14	0.0
3500 Å	47	0.83	<b>21</b>	12	4.0	14	0.0
3500 Å	<b>2</b>	<b>2</b>	61	10	1.4	9.8	0.0
3500 Å	<b>2</b>	4	<b>64</b>	9.0	2.1	12	0.0

<sup>a</sup> The time is that for disappearance of active chlorine. <sup>b</sup> Conversions into  $\epsilon$ -caprolactone and 3-chlorocyclohexanone were 0.0 under all conditions tried.

Registry No.—Cyclobutanone, 1191-95-3; cyclohexanone, 108-94-1; 4-chlorocyclohexanone, 21299-26-3; 3-chlorocyclohexanone, 21299-27-4; 6-chlorohexanoic acid, 4224-62-8.

Acknowledgments.—We are grateful to the Research Corporation for support of this work. Thanks are due to Miss A. M. Costello and Mrs. S. S. Kalbag for valuable technical assistance.

## Ion Radicals. XVIII. Reactions of Thianthrenium Perchlorate and Thianthrenium Trichlorodiiodide<sup>1,2</sup>

## Y. MURATA<sup>3</sup> AND H. J. SHINE

Department of Chemistry, Texas Technological College, Lubbock, Texas 79409

Received February 24, 1969

The crystalline perchlorate and trichlorodiiodide of the thianthrene cation radical,  $C_{12}H_8S_2$  +ClO<sub>4</sub><sup>-</sup>, and  $C_{12}H_8-S_2$  +I<sub>2</sub>Cl<sub>3</sub><sup>-</sup>, have been prepared. With these salts it has been possible to study the reactions of the thianthrene cation radical with water, iodide ion, chloride ion, triphenylamine, and, to some extent, the vinyl monomers styrene,  $\alpha$ -methylstyrene, ethyl vinyl ether, 1,1-diphenylethylene, acrylonitrile, and methyl methacrylate. Electron transfer to the thianthrene cation radical is facile, depending on the relative redox potentials of the cation radical and the other reactant. The reaction of the perchlorate salt with water has been studied in detail. The products are equal amounts of thianthrene and thianthrene 5-oxide. Kinetic work shows that the water reacts with the dication, formed by disproportionation of the cation radical, rather than with the cation radical itself. The longer known reactions of the thianthrene cation radical in sulfuric acid solution are now clearly understandable.

Cation radicals of thianthrene and similar compounds are usually obtained in concentrated sulfuric acid solution<sup>4,5</sup> although high-resolution esr spectra have been

(1) (a) Part XVII: H. J. Shine and Y. Murata, J. Amer. Chem. Soc., 91, 1872 (1969). (b) A report on the preparation of the trichlorodiiodide has been made: Y. Murata, L. Hughes, and H. J. Shine, Inorg. Nucl. Chem. Lett., 4, 573 (1968).

(2) Support by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-68-1359, is gratefully acknowledged.

(3) Postdoctoral fellow, 1967-1968.

(4) H. J. Shine and L. Piette, J. Amer. Chem. Soc., 84, 4798 (1962).

obtained recently with the nitromethane-aluminum chloride method at low temperatures.<sup>6,7</sup> Solid salts of the thianthrenium and similar cations are uncommon. Lucken has prepared thianthrenium perchlorate and pentachloroantimonate.<sup>8</sup> The latter has also been prepared by Kinoshita.<sup>9</sup> Both authors have discussed the

- (5) H. J. Shine, C. F. Dais, and R. J. Small, J. Org. Chem., 29, 21 (1964).
- (6) H. J. Shine and P. D. Sullivan, J. Phys. Chem., 72, 1390 (1968).
- (7) P. D. Sullivan, J. Amer. Chem. Soc., 90, 3618 (1968).
- (8) E. A. C. Lucken, J. Chem. Soc., 4963 (1962).
  (9) M. Kinoshita, Bull. Chem. Soc. Japan, 35, 1137 (1962).