

## Decompositions of Some Alkyl Hypochlorites

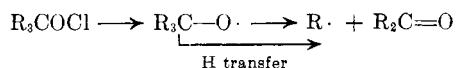
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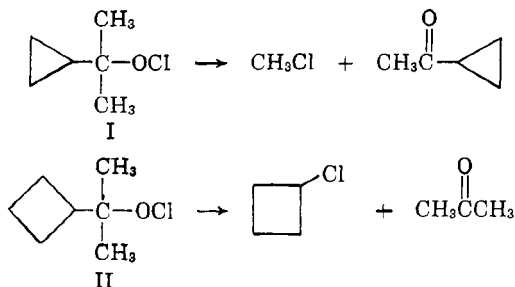
Thermal decomposition of cyclopropyldimethylcarbinyl hypochlorite yields methyl chloride and methyl cyclopropyl ketone. Similar decomposition of cyclobutyldimethylcarbinyl hypochlorite yields cyclobutyl chloride and acetone. These results suggest the following order of radical stability: cyclobutyl > methyl > cyclopropyl. Decomposition of cyclopropylcarbinyl hypochlorite yielded cyclopropylcarbinyl cyclopropanecarboxylate as the major product. Cyclobutyl hypochlorite decomposed to give a mixture of cyclobutyl  $\gamma$ -chlorobutyrate and  $\gamma$ -butyrolactone.

Recent studies by Greene and co-workers<sup>2</sup> and Walling and Padwa<sup>3</sup> have shown that *t*-alkyl hypochlorites provide a convenient source of a variety of free radicals. The thermal and light-initiated decompositions of these hypochlorites involve as a key intermediate the appropriate alkoxy radical,  $R_3C-O\cdot$ . In general, if the alkoxy radicals are formed in an inert medium, they de-



compose by loss of  $R\cdot$  and formation of a ketone and/or by intramolecular hydrogen transfer.

As part of studies of some ionic reactions of hypochlorites,<sup>4</sup> cyclopropyldimethylcarbinyl hypochlorite (I) and cyclobutyldimethylcarbinyl hypochlorite (II) were prepared. It was necessary to study their radical decompositions since it seemed inevitable that some of these would occur during the ionic reactions. The thermal decompositions of these substances in carbon tetrachloride were remarkably clean. The major products from I were methyl chloride and cyclopropyl methyl ketone. Decomposition of II under the same

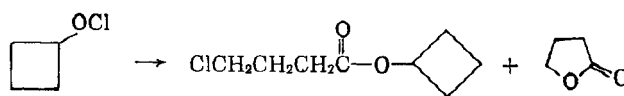


conditions yielded cyclobutyl chloride and acetone as the major products. It is quite clear that the decompositions of the two intermediate alkoxy radicals are remarkably specific and proceed in the main by loss of an alkyl group. The ease of loss of an alkyl group from a *t*-alkoxy radical reflects to some degree the stability of the radical which is being formed.<sup>2,3</sup> Thus a wide variety of cases has led to the following order of ease of loss and, therefore, by inference, radical stability: methyl < primary alkyl < secondary < tertiary.<sup>5</sup> Phenyl is lost more slowly than methyl.<sup>3</sup> Using this simple concept one arrives at the following order of radical stability: cyclobutyl > methyl > cyclopropyl.

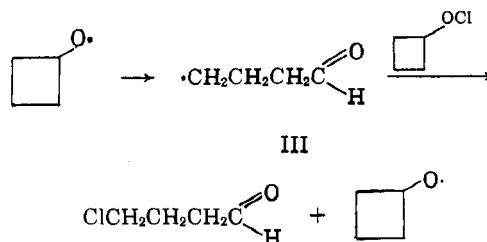
A similar conclusion regarding the stability of a cyclopropyl radical has been arrived at by Hart and Wyman.<sup>6</sup>

Very little information is available on the nature and reactions of primary and secondary hypochlorites. This is probably due in part at least to their reputation for being exceedingly delicate substances with a tendency to undergo quite spectacular decompositions.<sup>7</sup> Studies in this laboratory with several primary hypochlorites indicate that they are fairly stable in solution and no difficulty in handling has occurred.

Cyclobutyl hypochlorite was decomposed by boiling a carbon tetrachloride solution for 15 min. Most



secondary hypochlorites give ketones and hydrogen chloride.<sup>7b</sup> Cyclobutyl hypochlorite did not give any detectable cyclobutanone. The major products were cyclobutyl  $\gamma$ -chlorobutyrate and  $\gamma$ -butyrolactone. It appears that a major reaction path for the cyclobutyl-alkoxy radical is ring opening to the butyraldehyde radical (III). Ring opening relieves strain and, therefore, can compete effectively with other processes that the alkoxy



radical might undergo, *i.e.*, hydrogen abstraction: Ester formation in the decomposition of primary hypochlorites has been observed by Jenner.<sup>8</sup> Presumably the aldehyde is involved as an intermediate; thus the formation of cyclobutyl  $\gamma$ -chlorobutyrate can be rationalized in this particular case.<sup>9</sup> The formation of  $\gamma$ -butyrolactone is not surprising, although there is no evidence available to establish its mode of formation.

(6) (a) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959), and references cited therein; (b) see also C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962), for a discussion of this point and other relevant matters.

(7) (a) F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923); (b) R. Fort and L. Denivelle, *Bull. soc. chim. France*, 1109 (1954).

(8) E. L. Jenner, *J. Org. Chem.*, **27**, 1031 (1962).

(9) A likely path involves conversion of the aldehyde to the acid chloride by reaction with hypochlorite. This process gives the parent alcohol, which then reacts with the acid chloride to give the ester.

(1) Rutgers Research Council Faculty Fellow, 1963-1964.

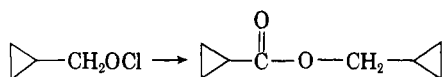
(2) F. D. Greene, *et al.*, *J. Org. Chem.*, **28**, 55 (1963).

(3) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593, 1597 (1963).

(4) (a) D. B. Denney and R. DiLeone, *ibid.*, **84**, 4737 (1962); (b) J. W. Hanifin, Jr., unpublished results.

(5) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

Cyclopropylcarbinyl hypochlorite decomposed rather cleanly to cyclopropylcarbinyl cyclopropanecarboxylate.



### Experimental<sup>10</sup>

**Materials.**—Cyclopropylcarbinol was prepared by lithium aluminum hydride reduction of cyclopropanecarboxylic acid.<sup>11</sup> Conversion to the acetate by reaction with acetic anhydride in pyridine followed by g.l.p.c. at 135° with a 10-ft. Carbowax 6 M column showed the material was essentially 100% pure.<sup>12</sup> Cyclobutanol was prepared by isomerization of cyclopropylcarbinol with hydrochloric acid.<sup>13</sup> Analysis of the acetate showed the material was 86% cyclobutanol, 8% cyclopropylcarbinol, and 6% allylcarbinol. Cyclobutanone was prepared by oxidation of this material.<sup>13</sup> Dimethylcyclobutylcarbinol<sup>14</sup> was prepared by allowing methylmagnesium iodide to react with ethyl cyclobutanecarboxylate. The properties were in accord with those reported. The n.m.r. spectrum on the liquid had a peak at 6.4 (hydroxyl), 8.9 (methyl), and a complex pattern centered at 8.1  $\tau$  (cyclobutyl). The ratio of areas was 1:6:7. Dimethylcyclopropylcarbinol<sup>13b,15</sup> was prepared by allowing methylmagnesium iodide to react with methyl cyclopropyl ketone. The properties were in accord with those reported. The n.m.r. spectrum had single peaks at 6.3 (hydroxyl), 8.7 (methyl), and a complex pattern centered at 9.5  $\tau$  (cyclopropyl). The ratio of areas was 1:6:5. The hypochlorites were prepared by treating a solution of the alcohol in carbon tetrachloride with excess hypochlorous acid solution. The hypochlorite solutions were washed with 10% aqueous sodium bicarbonate solution and dried with calcium chloride before decomposition.

**Decomposition of Dimethylcyclopropylcarbinyl Hypochlorite.**—The carbon tetrachloride solution was heated under reflux until the oxidizing power disappeared (determined by treating aliquots with potassium iodide solution followed by titration with thio-sulfate solution). A Dry Ice-acetone trap was used to collect evolved gases. The infrared spectrum of the solution after decomposition had a carbonyl band at 1710  $\text{cm}^{-1}$ . G.l.p.c. analysis, 10-ft. 6 M Carbowax column programmed from 60° at 7.5°/min., showed methyl cyclopropyl ketone was present and acetone was absent. A sample was collected by g.l.p.c. and shown to

(10) G.l.p.c. analyses were performed with an F & M Model 500 under the conditions specified. N.m.r. spectra were obtained with a Varian Associates Model A-60.

(11) C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

(12) Separation of cyclopropylcarbinol, cyclobutanol, and allylcarbinol was difficult by g.l.p.c. Thus recourse was had to analysis of the acetates.

(13) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(14) (a) B. A. Kazanskii, M. Yu. Lukina, and L. A. Nakhapetyn, *Dokl. Akad. Nauk SSSR*, **101**, 683 (1955); *Chem. Abstr.*, **50**, 3247 (1956); (b) G. Chiurdoglu and S. Van Walle, *Bull. soc. chim. Belges*, **66**, 612 (1957).

(15) V. A. Slabey and P. H. Wise, *Natl. Advisory Comm. Aeronautics, Tech. Note*, 2258 (1951); *Chem. Abstr.*, **45**, 7531 (1951).

have an infrared spectrum identical with that of methyl cyclopropyl ketone. G.l.p.c. analysis of the material collected in the cold trap showed it to be methyl chloride. Retention time (1.8 min.) was identical with that of a known sample on the 10-ft. 6 M Carbowax column at 50°.

**Decomposition of Dimethylcyclobutylcarbinyl Hypochlorite.**—The carbon tetrachloride solution of the hypochlorite was heated under reflux until the oxidizing power disappeared. G.l.p.c. analysis at 70° with a 10-ft. 6 M Carbowax column showed acetone and cyclobutyl chloride were the only major volatile products. These results were confirmed by g.l.p.c. analysis at 70° with a 10-ft. trioctyl trimellitate column. With both columns the retention times of the two components were identical with those of acetone and cyclobutyl chloride. Addition of acetone and cyclobutyl chloride to the reaction mixture increased the size of the peaks originally present.

**Decomposition of Cyclopropylcarbinyl Hypochlorite.**—The carbon tetrachloride solution was heated under reflux until the oxidizing power disappeared. The carbon tetrachloride was removed by distillation through a spinning band column. The residue gave a slight test with 2,4-dinitrophenylhydrazine. G.l.p.c. analysis, 10-ft. 20 M Carbowax column at 140°, showed there was one major component with only minor contamination. A sample was collected; it had ester absorption in the infrared at 1750  $\text{cm}^{-1}$ . The n.m.r. spectrum had a doublet at 6.1 (methylene) and cyclopropyl hydrogens centered at 9.2  $\tau$ ; the ratio of areas was 1:5.

**Decomposition of Cyclobutyl Hypochlorite.**—The infrared spectrum of the carbon tetrachloride solution after decomposition had carbonyl absorptions at 1800 and 1740  $\text{cm}^{-1}$ . The carbon tetrachloride was removed by distillation through a spinning band column, and the residue was analyzed by g.l.p.c. using a 10-ft. 20 M Carbowax column at 165°. Two major peaks, retention times 10.2 min. and 13.0 min., were found.  $\gamma$ -Butyrolactone under the same conditions had retention time 10.2 min. and cyclobutyl  $\gamma$ -chlorobutyrate had 13.0 min. G.l.p.c. analysis on a 10-ft. 6 M Carbowax column at 185° again showed two major peaks, retention times 9.4 and 12.3 min., which are the same as those found for  $\gamma$ -butyrolactone and cyclobutyl  $\gamma$ -chlorobutyrate. Samples were collected by g.l.p.c. and their infrared spectra were found to be identical with those of  $\gamma$ -butyrolactone and cyclobutyl  $\gamma$ -chlorobutyrate.

**Cyclobutyl  $\gamma$ -Chlorobutyrate.**—Cyclobutanol, 1.0 g. (0.014 mole), in 12 ml. of anhydrous pyridine was treated with 2.0 g. (0.014 mole) of  $\gamma$ -chlorobutyryl chloride. The mixture was heated briefly and then acidified with dilute hydrochloric acid. The aqueous solution was extracted with two 25-ml. portions of ether which were combined, washed with dilute sodium bicarbonate solution, and dried over calcium chloride. The ether was evaporated. The infrared spectrum had a carbonyl band at 1740  $\text{cm}^{-1}$ . The n.m.r. spectrum had a quintet at 5.04 (tertiary cyclobutyl hydrogen), a triplet at 6.42 ( $-\text{CH}_2\text{Cl}$ ), and a complex pattern at 7.88  $\tau$ . The ratio of areas was 1:2:10.

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