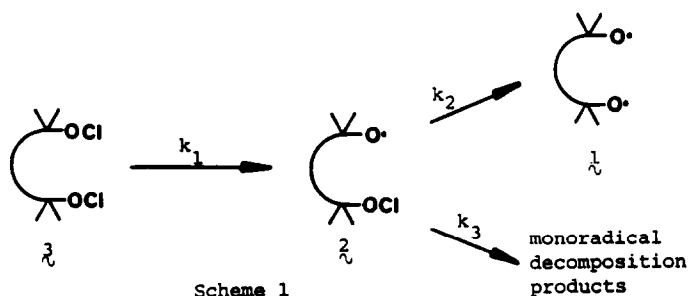


ON THE THERMAL DECOMPOSITION OF 2,5-DIHYPPOCHLORO-2,5-DIMETHYLHEXANE

J. Arce de Sanabria,* L.M. De Cárdenas, and N. Quirós Méndez
Department of Chemistry
University of Puerto Rico
Río Piedras, Puerto Rico 00931

SUMMARY: The title compound was prepared, characterized, and on thermal decomposition at 100°C in the presence of a chlorine atom trap was found to give acetone, 1,2-dichloroethane, and 4-chloro-2-methyl-2-butanol.

Dioxo diradicals $\overset{\cdot}{\text{O}}-\text{O}$ have been postulated as intermediates in most cyclic peroxide decompositions¹ while in others the fragmentation of the O-O bond is not the principal mode of reaction.² In our interest of generating dioxo diradicals from alternate sources, we have investigated the possibility of utilizing heretofore unknown organic dihypochlorites as precursors since monohypochlorites have been extensively utilized as efficient generators of alkoxy radicals.³ To successfully generate a dioxo diradical from a dihypochlorite it is essential that $k_2 > k_3$ as shown in Scheme 1.

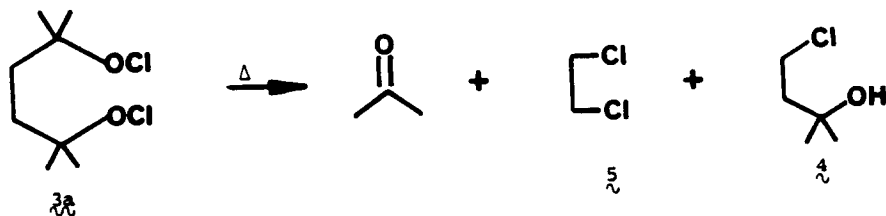


This condition could be achieved by increasing the stability of alkoxy radical $\overset{\cdot}{\text{O}}$, making it tertiary and with no available delta hydrogens to abstract. Tertiary organic hypochlorites have been shown to be more stable than secondary or primary and abstraction of a delta

hydrogen via a six member transition state has been shown to be the principal mode of decomposition if possible. A most suitable first choice with these characteristics is 2,5-dihypochloro-2,5-dimethylhexane (3a). In addition, the study of the generation of the corresponding dioxo diradical 1a from this source is facilitated by the fact that 1a is known and its behavior has been thoroughly studied.⁴

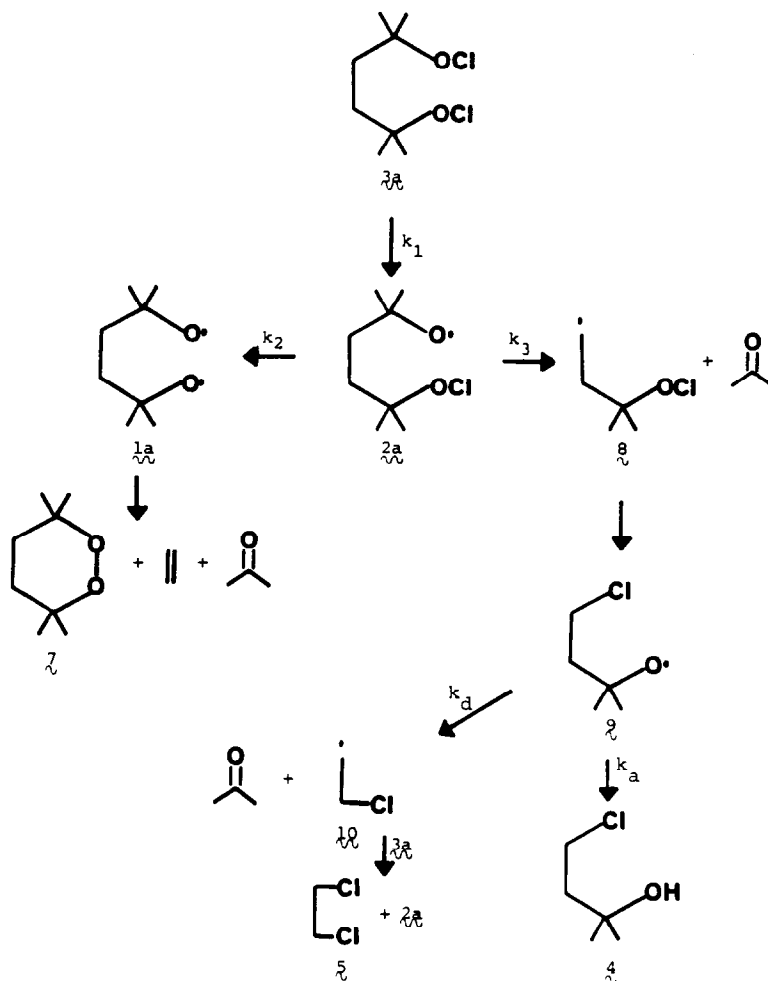
The title compound was prepared by the normal procedure followed in the preparation of monohypochlorites treating the corresponding diol with a 5% sodium hypochlorite solution in acetic acid with CCl_4 or pentane as solvent. The slightly yellow compound, obtained in quantitative yield, was characterized by its spectral properties: IR shows no -OH band; $^1\text{H-NMR}$ (CCl_4) δ 1.28 (s,3) and 1.61 (s,1); $^{13}\text{C-NMR}$ (CDCl_3) δ 25.7, 33.6 and 85.2; Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{O}_2\text{Cl}_2$: C, 44.67; H, 7.50; Cl, 32.96; Found: C, 45.01; H, 7.79; Cl, 32.63. In addition, low temperature reduction with lithium aluminum hydride or thermal decomposition in wet pentane regenerates the original 2,5-dimethyl-2,5-hexanediol. Compound 3a has been handled with no problem at room temperature, but is sensitive to light. It can be stored in solution at 10° in an amber bottle for several months without appreciable decomposition. Since, to the best of our knowledge, this is the first known organic dihypochlorite we wish to report on its thermal behavior.

The thermal decomposition of a 1.0 M solution of 3a in carbon tetrachloride or benzene, with added trichloroethylene (.1 M) as chlorine atom trap, was done in the dark in a sealed and degassed ampoule under nitrogen at 100°C . The dihypochlorite was completely decomposed in three hours under these conditions. The products were analyzed qualitatively and quantitatively by glpc and shown to be acetone, 1,2-dichloroethane (5), and 4-chloro-2-hydroxy-2-methylbutane (4) formed in a 4:1.5:1 molar ratio in CCl_4 and in a 6.4:2.6:1 molar ratio in benzene solvent as shown in Scheme 2. Control experiments in which the decomposition of the dihypochlorite 3a was done in the presence of 3,3,6,6-tetramethyl-1,2-dioxane (7) showed this dioxane to be completely stable to the actual thermolysis conditions.



Scheme 2

The products are formed in 86-88% relative yield and 4-6% is accounted as involatile residue establishing over 90% product balance. The absence of 3,3,6,6-tetramethyl-1,2-dioxane (7), and the presence of only traces of ethylene precludes the formation of the 1,6-diradical $\underline{1a}$ from $\underline{3a}$, since $\underline{1a}$ has been shown to quantitatively give these products when thermally generated.⁴ A mechanism that best accommodates these results is presented in Scheme 3.



The first step in the thermal decomposition of $\underline{3a}$ must be the cleavage of an O-Cl bond. The rate of alpha-scission (k_3) must be faster than the rate for the second O-Cl bond cleavage (k_2) and intermediate $\underline{8}$ is formed. Monoradical $\underline{8}$ is chlorinated intramolecularly to

generate alkoxy radical 9. Radical 9 subsequently loses acetone to generate radical 10 which initiates then a radical chain reaction by intermolecular chlorination by a dihypochlorite to give 1,2-dichloroethane (5) or abstracts a hydrogen atom to give chlorohydrin 4. The solvent effect that we have found affecting the relative ratio of hydrogen abstraction vs. scission of the alkoxy radical 9 is similar to the one that has been observed with the monoalkoxy radicals generated from monohypochlorites.⁵ The participation of a chlorine atom chain reaction^{3c} is ruled out since only traces of 2,5-dimethyl-2,5-hexanediol is formed, which should have been a principal product if such a radical chain reaction had occurred.

Other dihypochlorites with structural variations are being studied and so far found to behave thermally and photochemically in a similar manner.

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