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EPOXIDATION OF OLEFINS BY HYDROGEN PEROXIDE IN THE PRESENCE OF TETRACHLOROACETONE

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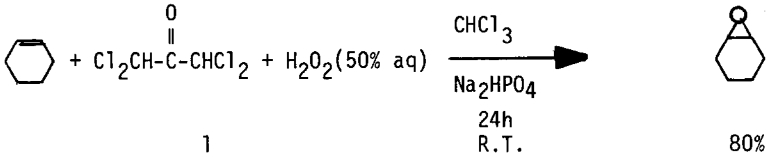
Abstract: 1,1,3,3-Tetrachloroacetone, an inexpensive, commercially available material, has been shown to be effective in mediating the hydrogen peroxide oxidation of a variety of olefins to epoxides. The chloroacetone is readily recovered for re-use.

Hexafluoroacetone has been shown by Kim to be a reagent capable of mediating the hydrogen peroxide oxidation of olefins to epoxides in good yield.[1] More recently, Ganem and Heggs utilized solutions of 2-hydroperoxy-hexafluoro-2-propanol to effect the epoxidation of olefins in high yield under mild conditions.[2]

Due to the commercial unavailability of hexafluoroacetone and its high toxicity, [3,4] a number of α-chlorinated compounds were screened for their ability to promote epoxidation of cyclohexene with aqueous hydrogen peroxide. In general, low yields of epoxide were observed; but in one case involving 1,1,3,3-tetrachloroacetone, 1,[5] cyclohexene was totally consumed in a short period of time. Cyclohexane, 1,2-diol was identified as a reaction product. Addition of solid Na_2HPO_4 to the reaction mixture allowed the isolation of cyclohexene oxide. By adjusting the relative amounts of reactants, buffer, and solvent, an 80% yield of epoxide was realized (eq.1). Based only upon unreacted starting material and product epoxide, the material balance was 85%

(eq.1)



$$+ Cl_2CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}CHCl_2 + H_2O_2(50\%\ aq) \xrightarrow[Na_2HPO_4]{CHCl_3}$$

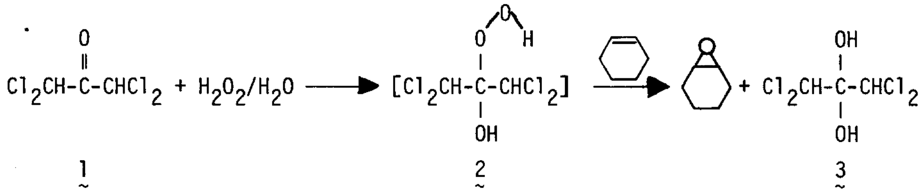
1

80%

Total consumption of olefin could be effected through use of longer reaction times or larger amounts of α-haloketone and hydrogen peroxide.

It is assumed that the reaction proceeds through formation of 2-hydroperoxy-1,1,3,3-tetrachloro-2-propanol, 2, which serves as the actual oxidant (eq.2). In the course of epoxidation, tetrachloroacetone hydrate 3 is formed as a by-product. It is probably 3 that necessitates the addition of buffer, since geminal diols produced from hexafluoroacetone and tetrafluoroacetone display appreciable acidity (pKa 6.6 and 8.8, respectively).[6]

(eq.2)



Several olefins have been successfully epoxidized under conditions similar to those reflected in eq.1; the results of these epoxidations appear in Table I.

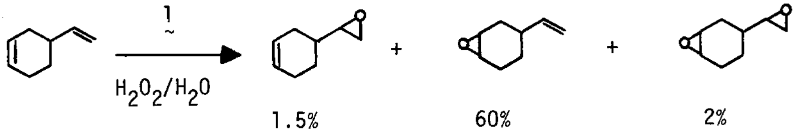
TABLE I

Epoxidation of Olefins with H_2O_2 in the Presence of 1.

Olefin	Epoxide % yield by VPC	Olefin % recovery by VPC	Epoxide % isolated
cyclohexene	71	trace	44
cyclooctene	83	trace	67
β-methylstyrene	77	1	49
2-methyl-1-hexene	81	trace	56
2,4,4-trimethyl-1-pentene	75	13	38
1-methylcyclohexene	75	trace	55
2,4,4-trimethyl-2-pentene	64	trace	57
2-methyl-2-pentene	80	5	57

Under the conditions used, higher temperatures effect a faster reaction, but result in reduced yields of epoxide. Solvent choices are limited. Of those tried, only chloroform, dichloromethane, benzene, and toluene appear to allow for successful oxidation. However, the reaction may be run without solvent when the olefin is a liquid, with only slightly diminished yields. Aqueous hydrogen peroxide of 30, 50, and 90% concentration has been successfully utilized. The reaction appears to be stereospecific, since only trans-4-octene oxide is detected by either vpc or ^{13}C analysis when trans-4-octene is subjected to epoxidation conditions. Finally, monosubstituted olefins generally give only low yields of epoxides by this method. Of those tested, only 1-octene yielded the corresponding epoxide in greater than 20% (21%) yield. Epoxidation of 4-vinyl-cyclohexene illustrates the selectivity of the reaction (eq.3).

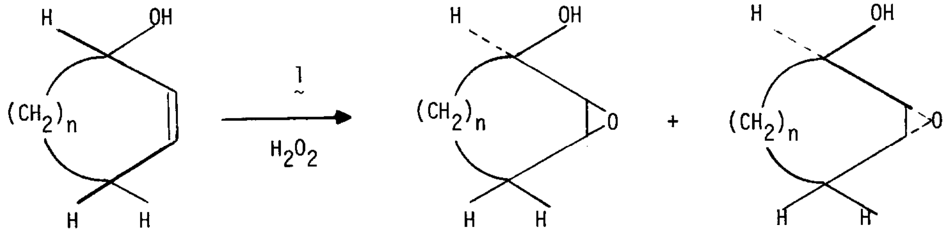
(eq.3)



Both 2-cyclohexen-1-ol 4a and 2-cycloocten-1-ol 4b were subjected to epoxidation conditions, in order to ascertain the effect of a neighboring hydroxyl group on the stereochemistry of epoxidation. The epimer distributions qualitatively resemble those produced by epoxidations of 4a and

4b with MCPBA and are in contrast to the results obtained by transition metal-catalyzed hydroperoxide oxidations.[7]

(eq.4)



4 5 6

	Ratio 5:6	Combined Yield
4a, n = 2	68:32	50%
4b, n = 4	<0.5:>99.5	93%

In a typical experiment, **1** (9.41g, 0.048 mol) and 50% H_2O_2 (4.2 mL, 0.074 mol H_2O_2) were mixed and stirred until homogeneous, then 5 mL $CHCl_3$ and 0.86g (0.006 mol) solid Na_2HPO_4 was added. 2-Methyl-1-hexene (4.7g, 0.48 mol) was added all at once; transfer was aided with a small amount of $CHCl_3$. The reaction mixture was stirred for 16 h at ambient temperature, after which time another 1.4 mL (approx. 0.024 mol H_2O_2) of aqueous peroxide was added. After 24 h, the mixture was poured into 30 mL pentane and the aqueous layer removed. The organic layer was washed with three, 50 mL volumes of water, then stirred for 10 min with 30 mL of 6N NaOH. Afterwards, the organic phase was washed with saturated $NaHSO_3$, dried with $MgSO_4$ and condensed. The yields are shown in Table I. Analysis of isolated material by IR, ^{1}HNMR, ^{13}CNMR and elemental analysis confirmed the identity of the product.

It is important to emphasize that although most of the haloacetone can be removed by two or three water washes of the organic layer, the final amount must be removed by treating the reaction mixture with either a dilute Na_2CO_3 or NaOH solution. If this is not done, the product epoxides decompose during attempted distillation when pot temperatures exceed 100°C.

A significant feature of the present method is recovery and recycle of the tetrachloroacetone. Discovery of the thermal instability of the hydrate **3** allowed for the development of a simple recovery procedure for **1** from the aqueous extracts, where it presumably exists as **3**. Flash evaporation of the water at elevated temperatures prevents sublimation of the hydrate and effects the rapid removal of water. Final amounts of water may be removed by azeotropic distillation with hexane, which itself is subsequently flashed off. Generally, greater than 70% of **1** may be recovered in this way.

By again taking advantage of the thermal instability of **3**, it has been possible to devise a reaction catalytic in **1**. A 40% yield of cyclooctene oxide can be attained within 4 h from a refluxing solution of cyclooctene, two equivalents of 50% hydrogen peroxide, 0.2 equivalents of **1**, and chloroform. After 24 hours, the conversion to epoxide is greater than 95%. An improvement in reaction rate can be effected if water is continuously removed via azeotrope from the reaction mixture; in this way, an 83% yield of cyclooctene oxide was produced in only 4 h. In such cases the peroxide solution is added incrementally. Buffer may be deleted in these reactions, presumably due to the low concentration of 3 at any instant in time.

References

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