

Some Recent Developments on the Synthesis, Chemical Reactivity, and Theoretical Studies of Tetroxanes

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ABSTRACT

The authors present a review on some recent developments on the synthesis, chemical reactivity and theoretical studies of Tetroxanes analysing their main physical chemistry properties. The authors examine the critical points of the PES of different conformers, and reaction paths at singlet ground state and triplet state of the tetroxane, leader member of the cyclic diperoxide compound family.

Keywords: Chemical Reactivity, Synthesis, Synthetic Methods, Tetroxanes, Theoretical Calculations

INTRODUCTION

The synthesis and reactivity of cyclic peroxides have attracted the attention of many investigators (Schulz, 2000; Cafferatta et al., 1984, 1986, 1990, 1991, 1995; Jorge et al., 1994, 1999, 2000, 2001, 2002, 2002; Leiva et al., 1998, 2001; Castellanos et al., 2000; Romero & al., 2005; Gelancha et al., 2004; Oxley et al., 2002; Dubvikova et al., 2005; Hong & Lin, 1996), due to the particular reactivity of the O-O bond.

Cyclic diperoxides have been used as efficient sources of radicals for the initiation of radical polymerization reactions (Lockley et al., 2000; Barreto & Eyler, 2007; Cañizo et al., 2004) and the role of cyclic peroxides in the biosynthesis of prostacyclines and thromboxanes is well documented (van Dorp, 1979). Appropriately substituted 1,2,4-trioxanes and 1,2,4,5-tetroxanes display significant antimalarial activities (Jefford et al., 1988, 2000; Vennerstrom et al., 1992, 2000; Posner et al., 1998, 2001; Li et al., 2000; Dechy-Cabaret et al., 2002). Within the realm of biological systems they are particularly

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important since they take part in transformations associated with cellular decaying, produced by enzymatic self-oxidations due to some peroxidic species.

Several reaction of the decomposition (Cafferatta et al., 1984, 1986, 1990, 1991, 1995; Jorge et al., 2000, 2002; Eyler et al., 1993, 1999, 2000, 2002), thermochemical (Eyler et al., 1999; Murray et al., 1966; Wulz et al., 1970) and quantum-chemical (Jorge et al., 1994, 1999, 2000, 2001, 2002, 2002; Leiva et al., 1998, 2001; Castellanos et al., 2000; Diez & Jubert, 2000) data sets for 1,2,4-trioxanes and 1,2,4,5-tetroxanes are available. Solvent effects on the inversion barrier of 3,3,6,6-tetramethyl-1,2,4,5-tetroxane (or dimeric acetone peroxide) have been studied (Brune et al., 1971) and a conformational analysis in the liquid phase suggested that the chair conformer is more stable than the twist form (Murray et al., 1966). Although dimeric acetone peroxide has been known for more than 100 years, the crystal structure has been reported for Gelancha et al. in 2004. Groth (1967a, 1967b) reported structures of several dimeric peroxides, but dimeric ac-

etone diperoxide was left undetermined because of a twinning problem.

The aim of the present review work was to provide a complete analysis of the family of 1,2,4,5-tetroxanes, in order to report the findings obtained from experimental reactivity, physicochemical properties and those derived from studies of chemistry quantum calculations.

PREPARATIVE METHODS

The ketone and aldehyde diperoxide (Figure 1 and Figure 2) of the type illustrated in Scheme 2 was prepared from the acid catalysed oxidation of different types of ketones or aldehydes with hydrogen peroxides (about 60% concentration) at temperatures below -10°C (Scheme 1) (Cafferatta et al., 1984, 1986, 1990, 1991, 1995; Jorge et al., 2000, 2001, 2002; Leiva et al., 2001).

The compounds obtained in this way were purified by recrystallization and the purity checked by CG and IR analyses.

The molecular configuration of tetroxanes with various substituent groups can be, cis or

Figure 1. Acid catalysed oxidation of different types of ketones or aldehydes with hydrogen peroxides (about 60% concentration) at temperatures below -10°C

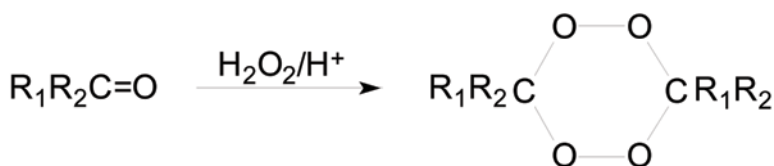
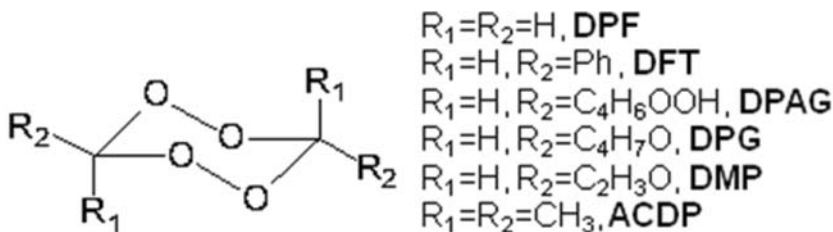


Figure 2. Ketone and aldehyde diperoxide



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