

ADAMANTYLIDENEADAMANTANE PEROXIDE,

A STABLE 1,2-DIOXETANE.

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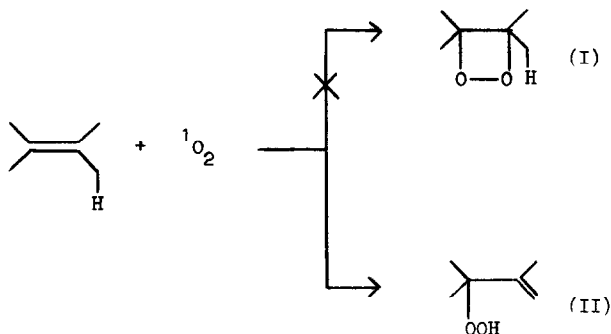
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(Received in UK 23 November 1971; accepted for publication 9 December 1971)

Proposed intermediates in bromine and chlorine addition reactions to olefins were stabilized when adamantylideneadamantane (III) was the substrate.^{1,2} This unique property of the adamantane moiety warrants further study.

Singlet oxygen has the property of adding to electron rich olefins to form 1,2-dioxetanes as the principal products.³ Reasonably stable tetramethoxy- and 3,4-dimethoxy-1,2-dioxetanes have been obtained in the photooxygenation of tetramethoxyethylene⁴ and 1,2-diethoxyethylene⁵ respectively. Attempts to cycloadd singlet oxygen to olefins bearing allylic hydrogens, in order to prepare alkylated 1,2-dioxetanes (I), resulted in the formation of allylic hydroperoxides of rearranged structure (II).^{6,15}



$^1\text{H-NMR}$ -spectrum (CCl_4): complex multiplet at $\tau = 7,75-8,70$ (24H) and complex multiplet at $\tau = 7,25-7,60$ (4H).

$^{13}\text{C-NMR}$ -spectrum⁸ (CCl_4): in accordance with the proposed peroxide structure.⁹

The elemental analysis and molecular weight (osmometrical) are in accordance with the peroxide structure.

The thermal properties of the compound are also typical for a peroxide structure.

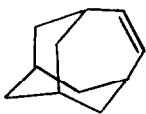
Heated above its melting point ($163-164^\circ$), IV explodes vigorously at about 240° , the product being adamantanone. Gentle heating in ethyleneglycol till reflux causes a beautiful, very bright chemiluminescence.^{10,11} Work up gave an 80% yield of pure adamantanone.

Conclusive chemical support for the 1,2-dioxetane structure of IV was found in the zinc/acetic reduction to V. This glycol, formed in 80% yield, was identical in all respects to that previously prepared in this laboratory.¹²

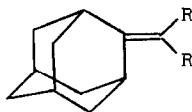
Several other reduction procedures failed to provide definitive structure proof:

- i. Treatment of IV with sodiumborohydride for 62 hrs. at room temperature gave only starting material.
- ii. Reduction of IV with LAH for 15 hrs. at room temperature led to quantitative formation of 2-adamantanol.
- iii. Catalytic hydrogenation with Pd/C gave a mixture of 2-adamantanol and adamantanone. Omission of hydrogen led only to adamantanone, indicating that the metal catalyzed the breakdown.

In sharp contrast to the behaviour of adamantylideneadamantane, olefins VI¹³, VIIa¹⁴, b⁹, c⁹ were inert under identical oxygenation conditions.



(VI)



(VII)

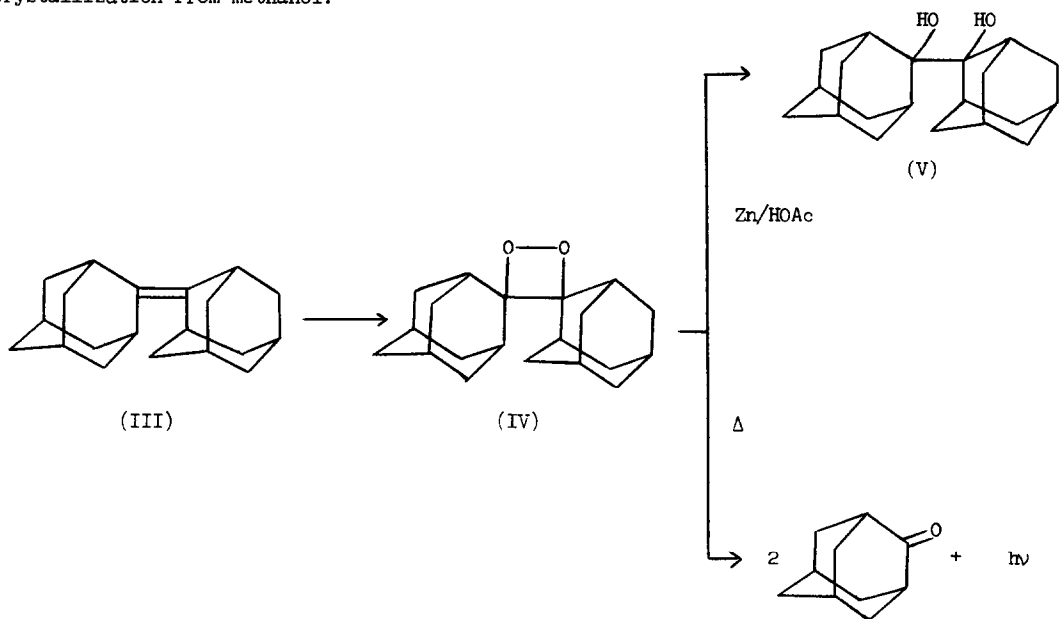
- a) R = H
- b) R = C_6H_5
- c) R = tert.- C_4H_9

To achieve this goal these conditions must be met:

- i. The olefin must be sufficiently electron-rich,
- ii. No allylic hydrogens must be available (the word allylic implies real allylic activity),
- iii. Steric hindrance should not inhibit the reaction.

We have found that adamantylideneadamantane (III) meets these three conditions in contrast to all other alkylated olefins studied thusfar.

When singlet oxygen was generated by Methylene Blue sensitization of molecular oxygen, the cyclic peroxide (IV) could be isolated by evaporation of the solvent after absorbing the dye on charcoal. Using the triphenylphosphite-ozone complex⁷ as source of singlet oxygen, the cycloadduct IV was readily isolated by column chromatography on florisil with carbontetrachloride as solvent. The yield in both cases must be nearly quantitative since 85% of pure material was obtained after recrystallization from methanol.



The cyclic peroxide (IV) exhibited the following spectral properties:

IR-spectrum: no carbonyl absorption, multiple strong absorptions at 1100, 1065, 1010, 1000, 975 and 923 cm^{-1} .

Mass-spectrum: no molecular ion at m/e 300 ($\Delta v = 70$ V, source: 170°); base peak at m/e 150 ($\text{C}_{10}\text{H}_{14}\text{O}^+$); peaks at m/e 284 ($\text{C}_{20}\text{H}_{28}\text{O}^+$) and at m/e 268 ($\text{C}_{20}\text{H}_{28}^+$).

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7. Q.E. Thompson, ibid., 83, 845 (1961).
8. We thank Dr. J. Lugtenburg and the staff of JEOL-USA for recording and interpreting this spectrum.
9. Details may be found in the forthcoming dissertation of J.H. Wieringa.
10. 1,2-Dioxetanes are known to luminesce on thermal decomposition. See refs. 4 and 5.
11. The elucidation of the thermochemistry and kinetics of the thermal decomposition of IV by DSC (differential scanning calorimetry) is in progress. See: W. Adam and J.C. Chang, Int. J. Chem. Kin., 1, 487 (1969).
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15. For recent analogous oxygenations in biological systems see H.W.-S. Chan, ibid., 93, 4632 (1971).