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A Novel Pathway in the Photooxygenation of Cyclic Allenes

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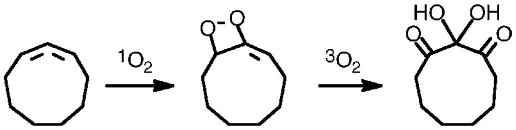
ABSTRACT

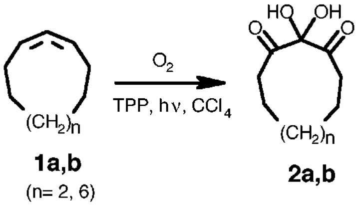


The photooxidation of cyclic allenes gives rise to cyclic 1,2,3-trione hydrates. The formation of these compounds points to a novel photooxidation mechanism involving both singlet and triplet oxygen. Upon placement of a methyl group on the allene, the mechanism shifts to predominantly an "ene" reaction. The corresponding cycloadditions with 4-methyl-1,3,4-triazoline-3,5-dione (MTAD) with cyclic allenes involve 2 equiv of MTAD. The dipolar intermediates are trapped with H_2O to give α-urazole-substituted 2-cycloalkenones.

Singlet oxygen ($^1O_2$) reacts with ordinary alkenes containing allylic hydrogens primarily by an "ene" mechanism leading to allyl hydroperoxides while electron-rich alkenes combine with $^1O_2$ mainly by way of a [2 + 2] cycloaddition to give 1,2-dioxetanes.[1] A previous report by Greibrokk[2] on allene photooxidations was revisited by Gollnick et al.[3] who showed that $^1O_2$ reacts with alkyl-substituted allenes[4] mainly by two pathways: a [2 + 2] addition followed by dioxetane cleavage to ketene and carbonyl components and an "ene" reaction whereby the resulting vinyl hydroperoxides rearrange to α-hydroxyketones and dienones. Our earlier studies in this area concerned the singlet oxygenations of arylallenes, which primarily react with $^1O_2$ by a Diels−Alder reaction with the phenylallenyl moiety.[5] We now report our results on the photooxidation of cyclic allenes, which have unveiled a surprising mode of singlet oxygen oxidations of olefins.

Upon irradiation with a 250 W sodium lamp at room temperature under a positive pressure of oxygen, and using tetraphenylporphyrin (TPP) as sensitizer, the cyclic allenes **1a** (C_9H_{14}) and **1b** ($C_{13}H_{22}$) slowly underwent photooxidation to give 1,2,3-trione hydrates **2a** and **2b** as major products in 73% and 68% isolated yields, respectively (Scheme 1).[6]

Scheme 1



Control experiments which were conducted either in the absence of sensitizer or in the presence of DABCO, a known singlet oxygen quencher,[7] revealed that $^1O_2$ was indeed the reactive species. Ring size had a profound effect on the

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[1] For reviews, see: (a) Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 173−242. (b) Bartlett, P. D.; Landis, M. E. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York 1979; pp 243−286. (c) Frimer, A. A. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley & Sons: New York, 1983; p 201.

[2] Greibrokk, T. *Tetrahedron Lett*. **1973**, 1663.

[3] (a) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett*. **1985**, *26*, 5029. (b) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett*. **1985**, *26*, 173. (c) Martinez, T. R. M.S. Thesis, San Francisco State University, San Francisco, CA, 1986.

[4] *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982; Vols. 1−3.

[5] Erden, I.; Martinez, T. R. *Tetrahedron Lett*. **1991**, *32*, 1859.

[6] Minute amounts (ca. 5%) of the corresponding "ene" products, hydroxyenones and dienones, are also formed in each case, along with polymeric material.

[7] Quannès, C.; Wilson, T. *J. Am. Chem. Soc*. **1968**, *90*, 6528.

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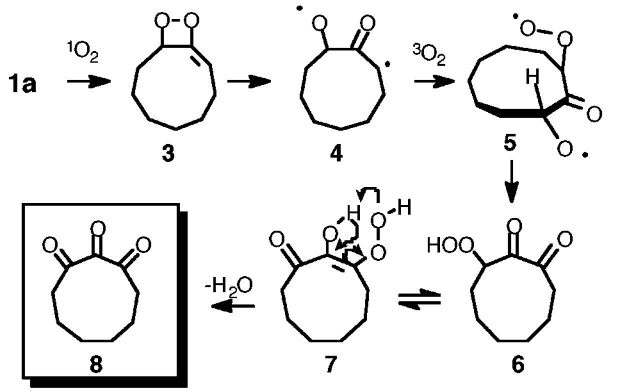
photooxygenation rates; the smaller ring allene reacted nearly six times as fast as the larger ring analogue.

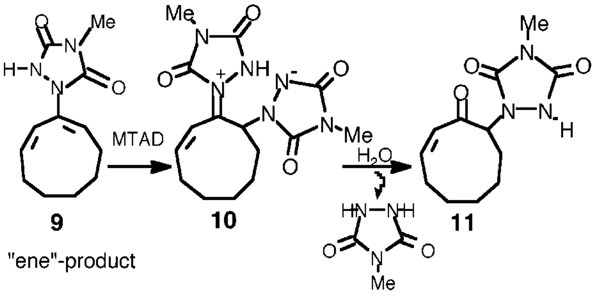
The oxidation of all three allenic carbons to carbonyl groups and the introduction of four oxygens in one synthetic step is remarkable. Although none of the postulated intermediates were isolable, the mechanism depicted in Scheme 2 appears to be entirely plausible and in accord with the experimental results. The photooxidation commences with a [2 + 2] cycloaddition of $^1O_2$ to the allene, followed by an O−O fission. However, the subsequent C−C cleavage, which is common in 1,2-dioxetane decompositions,[8] does not occur here due to the presence of the vinyl group at C2 in **3**. The carbonyl α-radical **4**, a resonance form of the initial enol radical, is captured by $^3O_2$. A 1,5-H shift to the peroxy radical ensues, affording an α-hydroperoxy ketone (**6**), which undergoes dehydration to give the trione **8**. The latter spontaneously hydrates at the central carbonyl group, as is common for 1,2,3-triones.[9]

Scheme 2



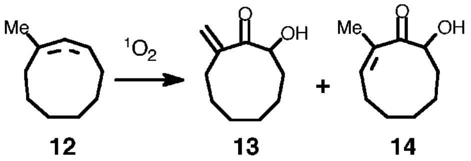
In view of the demonstrated similarities between $^1O_2$ and triazolinediones[10] in their reactivity patterns toward alkenes, we decided to probe the corresponding reactions of cyclic allenes with *N*-methyl-1,3,4-triazoline-2,5-dione (MTAD) in hopes of gaining further insight into the mechanism of the photooxygenations. Prior to our study, the reaction of diethyl azodicarboxylate with 1,2-cyclononadiene had been reported to give an "ene" product.[11] In our hands, treatment of **1a** with MTAD led to the formation of an intractable mixture in which polymeric material dominated. In hopes of trapping a possible zwitterionic intermediate, we conducted the reaction in THF in the presence of H_2O. In an earlier study we had reported the first example of a similar trapping reaction of a dipolar intermediate with H_2O during the cycloaddition of 4-phenyl-TAD to bicyclopropylidene.[12] In the present case, 2 equiv of MTAD was required for complete consumption of **1a**. A single product, **11**, was isolated from this reaction, the formation of which can be explained in terms of an initial "ene" reaction of MTAD with **1a** followed by a dipolar attack by a second equivalent of MTAD. The dipolar intermediate **10** is trapped with H_2O, and the resulting hemiaminal collapses to the carbonyl, affording enone **11** (Scheme 3).

Scheme 3



By contrast, 1-methylcyclonona-1,2-diene (**12**) reacted with $^1O_2$ under the same conditions significantly faster than its unsubstituted analogues, and the attack occurred selectively at the more highly substituted π-system, giving rise to both possible "ene" products, **13** and **14**, in a ratio of 2:3, respectively (Scheme 4). The observed regioselectivity is in line with the well-documented preference of $^1O_2$ for more highly substituted double bonds and is mainly due to electronic effects.[13]

Scheme 4



The reaction of **12** with 2 equiv of MTAD in the presence of H_2O produced a single trapping product, **15** (43%), along with a small amount of the "ene" products (8%) **16** and **17** (6:1 ratio, respectively) (Scheme 5).

Neither **16** nor **17** showed any tendency to react with a second equivalent of MTAD, presumably due to steric factors. The study presented above is of synthetic as well as mechanistic interest. Though acyclic vicinal triones have been

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[8] (a) Sara-Moeller, C. R.; Adam, W. In *Four-membered Rings with Two Oxygen Atoms: Dioxetanes*; Katritzky, A. R., Rees, C. W. E., Scriven, F., Eds.; Comprehensive Heterocyclic Chemistry, 2nd ed. (CHEC-2); Elsevier: 1996; Vol. 1, Chapter 1.33, pp 1041−1082. (b) Adam, W. In *The Chemistry of Functional Groups, Peroxides, Four-membered Ring Peroxides: 1,2-Dioxetanes and α-Peroxylactones*; Patai, S., Ed.; Wiley & Sons: New York, 1983; Chapter 24, pp 830−920.

[9] (a) Rubin, M. B. *Chem Rev*. **1975**, *75*, 177. (b) de Neufville, R.; von Pechmann, H. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3375.

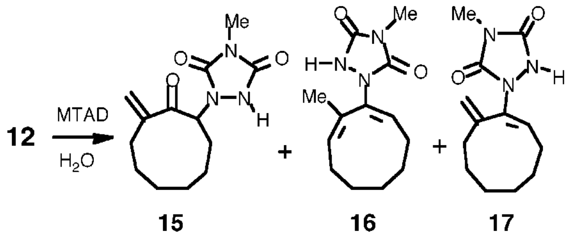
[10] Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659.

[11] (a) Lee, C. B.; Taylor, D. R. *J. Chem. Res., Synop*. **1977**, 136; *J. Chem. Res., Miniprint* **1977**, 1601. (b) Lee, C. B.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1463.

[12] de Meijere, A.; Erden, I.; Weber, W.; Kaufmann, D. *J. Org. Chem.* **1988**, *53*, 152.

[13] Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 287−427.

Scheme 5



prepared[14] and their role as important synthetic intermediates elegantly demonstrated by Wasserman et al.,[15] the cyclic analogues are more difficult to access synthetically, requiring 1,3-diketones as precursors in most cases.[16] The one-step synthesis of cyclic 1,2,3-triones (C ≥ 9) by photooxygenation of cyclic allenes described herein offers a convenient alternative to the existing methods by introducing all three oxygen functions in a single step from readily available starting materials. Moreover, the tandem $^1O_2/^3O_2$ addition to a 1,2-diene represents a pathway previously not observed in photochemical oxidations.

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Supporting Information Available: Experimental procedures and characterization data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] (a) Coats, S. J.; Wasserman, H. H. *Tetrahedron Lett*. **1995**, *36*, 7735. (b) Wasserman, H. H.; Baldino, C.; Coats, S. J. *J. Org. Chem*. **1995**, *60*, 8231.

[15] (a) Wasserman, H. H.; Shiraishi, M.; Cook, J. D. *Tetrahedron Lett*. **1995**, *36*, 6785. (b) Wasserman, H. H.; Blum, C. A. *Tetrahedron Lett*. **1994**, *35*, 9787. (c) Wasserman, H. H.; Lee, G. M. *Tetrahedron Lett*. **1994**, *35*, 9783. (c) Wasserman, H. H.; Vu, C. B. *Tetrahedron Lett*. **1994**, **35**, 9779. (d) Wasserman, H. H.; Kuo, G.-H. *Tetrahedron* **1992**, *48*, 7071 and references therein; (e) For a recent review on vicinal triones, see: Rubin, M. B.; Gleiter, R. *Chem Rev*. **2000**, *100*, 1121.

[16] (a) Schank, K.; Schuhknecht, C. *Chem. Ber*. **1982**, *115*, 3032. (b) Wasserman, H. H.; Pickett, J. E. *J. Am. Chem. Soc*. **1982**, *104*, 4695. (c) Mahran, M. R.; Abdou, W. M.; Sidky, M. M.; Wamhoff, H. *Egypt. J. Chem*. **1987**, *29*, 701. (d) Tatsugi, J.; Izawa, Y. *J. Chem. Res., Synop*. **1988**, 356. (e) Regitz, M.; Adolph, H. G. *Z. Naturforsch. B* **1968**, *23*, 1269. (f) Beck, E.; Hofmann, P.; Sieber, A. *Tetrahedron Lett*. **1981**, *22*, 4683.