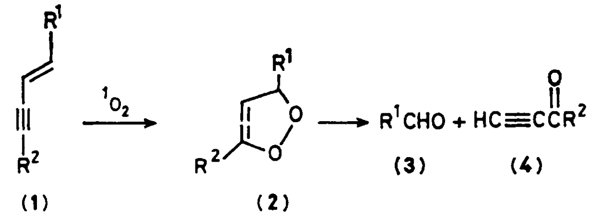
Singlet Oxygenation of But-1-en-3-ynes: on the Possible Intermediacy of a 1,2-Dioxacyclohexa-3,4-diene

Edward Lee-Ruff,* Mehran Maleki, Paul Duperrouzel, Min H. Lien, and Alan C. Hopkinson
Department of Chemistry, York University, Downsview, Ontario M3J 1P3, Canada

But-1-en-3-ynes undergo singlet oxygenation resulting in the formation of products rationalized as being derived from 1,2-dioxacyclohexa-3,4-dienes; *ab initio* calculations for such an intermediate are reported.

Additions to 1-en-3-ynes can proceed in a 1,4 manner giving substituted allenes.[1] Conversely, of the reported cycloadditions to 1-en-3-ynes only 1,2-cycloadditions are observed, addition occurring normally on the double bond portion of this functional group.[2] The strain associated with the formation of a six-membered cyclic allene[3] disfavours Diels–Alder reactions



a; $R^1 = R^2 = Ph$
b; $R^1 = p\text{-}MeOC_6H_4$, $R^2 = Ph$
c; $R^1 = OMe$, $R^2 = H$
d; $R^1 = R^2 = H$

Table 1. Yields of the oxygenation products (3) and (4).

Compound	Conditions	Yield (%) (3)	(4)
(**1a**)	$CHCl_3$	80[a]	84[a]
(**1b**)	$CHCl_3$	83[a]	85[a]
(**1b**)	CH_3OH	75[a]	80[a]
(**1c**)	$CHCl_3$[b]	70[c]	75[c] (dimethyl acetal)

[a] Isolated yields based on substrate. [b] Some methanol derived from the starting material was contained in this solution. [c] From integration of the ^1H n.m.r. spectrum.

in which such enynes act as 4π addends and to our knowledge no such reactions have been reported. Examples of intramolecular cycloaddition (electrocyclization) of a 1,3-dien-5-yne has been shown to occur photolytically;[4,5] however the experimental evidence points toward radical intermediates not involving cyclic allenes. We report that certain but-1-en-3-ynes will undergo 1,4-oxidations with singlet oxygen and that 1,2-dioxacyclohexa-3,4-dienes are likely intermediates in these transformations.

The 1,4-diarylbut-1-en-3-ynes (**1a**) and (**1b**) were prepared by literature methods.[6] The butenyne (**1c**) was a commercial sample (50% solution in aqueous methanol, Aldrich) and was used without further purification. Singlet oxygenations were carried out by passing a stream of oxygen through a solution containing the butenyne (**1a**—**c**) (0.05 M) and tetraphenylporphyrin (TPP) (20 mg) in chloroform (150 ml) while irradiating with a 500 W floodlight (G. E. Q 500 T3/CL Quartzline lamp). The samples were cooled by inserting the sample tubes in a water-cooled quartz immersion well (Hanovia) during irradiation. Reaction times varied from 8 h for (**1c**) to 75 h for (**1a**). For (**1a**) and (**1b**) the reaction proceeded cleanly to give the aldehydes (3) and ethynyl phenyl ketone (4) as the only products (Table 1). The ketone (4) had properties identical with those reported.[7] The enyne (**1c**) underwent singlet oxygenation to give methyl formate (**3c**) and prop-2-ynal dimethyl acetal which were not isolated owing to their volatility but were identified by comparison of the ^1H n.m.r. spectra of the photolysis mixture with those of authentic samples.[8] In order to confirm that singlet oxygen is the reactive agent in these transformations, control runs were carried out for (**1b**) in the absence of light and in another run in the absence of TPP. Both of these control experiments led to the recovery of starting material.

The formation of the oxidation products (3) and (4) can be best accounted for by postulating (2) as an intermediate. Whether such a species originates from a primary dioxetan or dioxete is not certain although in one reported case[9] of singlet oxygenation of an alkyne, an α-diketone was observed and rationalized as being formed from a dioxete. Attempts to isolate the cyclic peroxide (2) by low temperature reactions or trapping with methanol led to identical results indicating that the intermediate (2), if formed, preferentially undergoes the unimolecular cycloelimination process over any bimolecular reaction.

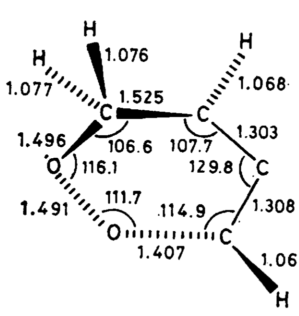


Figure 1. Calculated bond angles and distances for (**2d**).

In order to assess the stability of such cyclic peroxides, *ab initio* M.O. calculations were carried out for (**2d**). Using a 3–21 G basis set[10] and gradient optimisation methods[11,12] the singlet cyclic peroxide was shown to be at a minimum on the $C_4H_4O_2$ energy hypersurface. The ring is puckered with an inversion barrier of 27.9 kcal mol^{-1}.† The optimum bond lengths and bond angles are given in Figure 1. The ring opening reaction to form prop-2-ynal and formaldehyde is exothermic ($\Delta E = -62.9$ kcal mol^{-1})† at the 3–21 G level of theory. Thus the large exothermicity of this transformation as well as the weak O–O bond strength in (2)[13] appears to preclude bimolecular trapping of such derivatives.

Received, 3rd November 1982; Com. 1255

References

1 G. D. Melnikov, S. P. Melnikova, and A. A. Petrov, *J. Org. Chem. USSR*, 1982, 2339.
2 J. P. Gouesnard, *Tetrahedron*, 1978, **34**, 2083.
3 M. Balci and W. M. Jones, *J. Am. Chem. Soc.*, 1980, **102**, 7607; P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, 1974, **92**, 779.
4 A. H. A. Tinnemans and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1111.
5 A. H. A. Tinnemans and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1115.
6 A. H. A. Tinnemans and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1104. Mixtures of *cis*- and *trans*-(**1a**) and -(**1b**) with the *trans*-isomer predominating in both were used in these studies.
7 D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, 1972, **37**, 45.
8 The ^1H n.m.r. spectrum of prop-2-ynal showed all peaks shifted 0.3 p.p.m. to lower field from the reported values: P. S. Skell and R. F. Harris, *J. Am. Chem. Soc.*, 1969, **91**, 699. The nature of the solvent was not specified in this report.
9 C. S. Foote and J. W. P. Liu, *Tetrahedron Lett.*, 1968, 3267.
10 J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
11 P. Pulay, *Mol. Phys.*, 1969, **17**, 197; 1970, **18**, 473.
12 H. B. Schlegel, S. Wolfe, and B. Bernardi, *J. Chem. Phys.*, 1975, **63**, 3632.
13 E. J. Corey and H. Park, *J. Am. Chem. Soc.*, 1982, **104**, 1750. An estimate of 13 kcal mol^{-1} was assigned for the O–O bond strength in an acylic allenyl hydroperoxide.

---

† 1 cal = 4.184 J.