

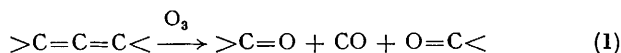
Reactions of Hindered Allenes with Ozone

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Summary Ozone has been shown to function as an oxygen transfer reagent with two hindered allenes leading to the formation of a cyclopropanone and an allene oxide as initial products.

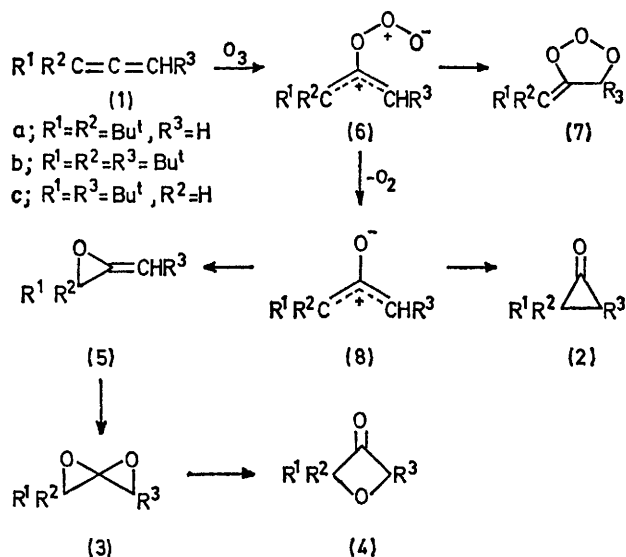
OZONE has been found to transfer oxygen to certain hindered olefins thereby producing epoxides.¹ This observation has prompted us to examine the reaction of this oxidizing agent with encumbered allenes as a potential synthetic pathway to the novel heterocycles, allene oxides.² The reaction of simple allenes has only recently been established to proceed to two carbonyl fragments and carbon monoxide by an unknown process which utilizes a single equivalent of ozone.³



The reaction of one equivalent of ozone with 1,1-di-*t*-butylallene (**1a**) in methylene chloride at -78° forms di-*t*-butyl ketone (62%) and 2,2-di-*t*-butylcyclopropanone⁴ (**2a**) (27%). Low-temperature n.m.r. observation of the reaction revealed that only (**2a**), di-*t*-butyl ketone, and formaldehyde accumulate in the reaction mixture. Cyclopropanone (**2a**) does react slowly under similar conditions to give di-*t*-butyl ketone but this conversion is much too slow to account for the formation of this ketone from (**1a**).

The addition of two equivalents of ozone to 1,1,3-tri-*t*-butylallene (**1b**) gave (**3b**) as the only significant product observed by n.m.r. at -78° . As expected (**3b**) rearranges cleanly into (**4b**) upon standing.² One equivalent of oxidant gave 41% of (**3b**) and 5% of allene oxide (**5b**) with consumption of only half of the (**1b**). The conversion of

(**5b**) into (**3b**) under similar conditions was independently demonstrated. This transformation evidently proceeds more rapidly than (**5b**) is formed from (**1b**).



By way of contrast, (**1c**) gave only pivaldehyde in its reaction with ozone. Low temperature n.m.r. monitoring was again unsuccessful in detecting a reaction intermediate.

These results can be accommodated within the framework of a reaction sequence initiated by electrophilic attack of

ozone at the central allenic carbon leading to (6). This dipolar species can ring-close to primary ozonide (7), the presumed intermediate for the conversion depicted by equation (1), or it can lose oxygen to yield stabilized zwitterion (8). This type of intermediate serves as the precursor to both (2a) and (5b) by alternate ring-closure processes. Cyclopropanone (2a) does not appear to be formed *via* allene oxide (5a), since (5a) has recently been observed in the peracid oxidation of (1a) and is stable for some time at

room temperature.⁵ Consequently (5a) should have been observed in the low temperature n.m.r. experiment. The features which determine the reaction mode of intermediate (6), are not presently understood.

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¹ P. S. Bailey, J. W. Ward, and R. E. Hornish, *J. Amer. Chem. Soc.*, 1971, **93**, 3552 and references therein.

² J. K. Crandall and W. H. Machleder, *J. Heterocyclic Chem.*, 1969, **6**, 777.

³ P. Kolsaker and B. Teige, *Acta Chem. Scand.*, 1970, **24**, 2102.

⁴ J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, 1968, **90**, 7347.

⁵ J. B. Komin, unpublished results.