# Reactions of Hindered Allenes with Ozone

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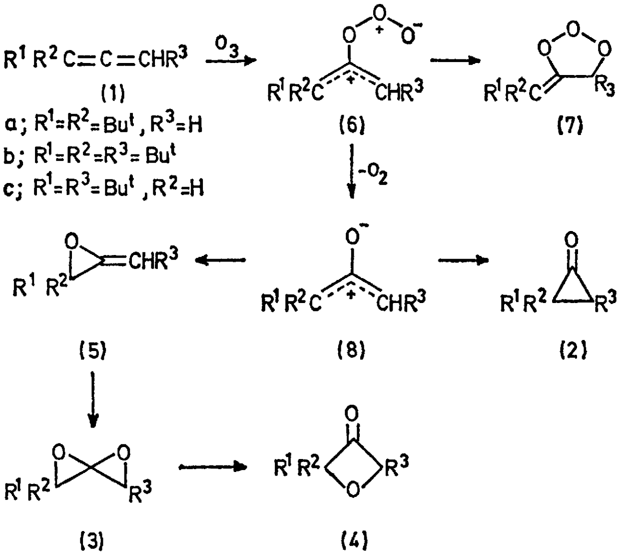
*Summary* Ozone has been shown to function as an oxygen transfer reagent with two hindered allenes leading to the formation of a cyclopropanone and an allene oxide as initial products.

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]

$$>C=C=C< \xrightarrow{O_3} >C=O + CO + O=C< \tag{1}$$

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-butylcyclopropanone[4] (**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. Kolsoker 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.