

Synthesis of an Allene Oxide

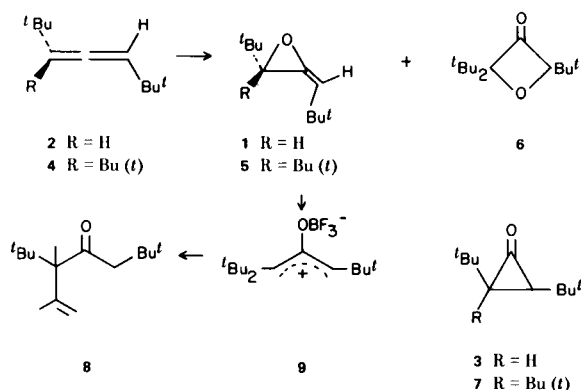
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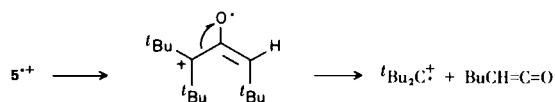
Earlier attempts in this laboratory to isolate an allene oxide from the peracid oxidation of an allene have been unsuccessful owing to the propensity of this reactive functional moiety to react with nucleophiles (3), undergo further epoxidation to an allene dioxide (4), and/or isomerize to the corresponding cyclopropanone (5). Recently, however, the first allene oxide **1** has been isolated from the epoxidation of 1,3-di-*t*-butylallene (2), and the valence isomerism of **1** to 2,3-di-*t*-butylcyclopropanone (**3**) has been demonstrated (6). In a concurrent study we have similarly prepared an intact allene oxide by the use of an allene precursor appropriately substituted with bulky groups.

Reaction of 1,1,3-tri-*t*-butylallene (**4**) with *m*-chloroperbenzoic acid generated a 10:1 ratio of two new materials whose structures are assigned as allene oxide **5** and oxetanone **6**, respectively. Oxetanone **6** [infrared, 5.56 μ ; nmr, τ 5.22 (1), 8.82 (9), 8.85 (9), and 8.97 (9); mass spectrum (14 eV), important fragments at *m/e* 184, 168, 154, 139, 111, 98, 85, and 57 (base)] is undoubtedly formed *via* an intermediate allene dioxide (3,4). Allene oxide **5** exhibits nmr absorption (carbon tetrachloride) as singlets at τ 5.41 and 8.90 in a 1:27 ratio. The addition of pyridine splits the high-field signal into a 2:1 doublet. Noteworthy is that the chemical shift of the olefinic proton is appropriate for the β -hydrogen of an enol ether (7). The infrared spectrum of **5** displays a medium-intensity band at 5.60 μ which is assigned to the C=C stretching mode. Methylene cyclopropanes and allene imines show analogous bands at 5.55 and 5.65 μ , respectively (8,9). The indicated stereochemistry of **5** is assigned on the presumption that peracid attack occurs from the less hindered side of the double bond as expected.



Allene oxide **5** is extraordinarily stable. It shows no tendency to react with nucleophiles and does not de-

tectably isomerize to cyclopropanone **7**. Despite evidence that allene oxides are transformed essentially completely to the corresponding cyclopropanones under mild conditions (5,6), the failure of **5** to isomerize to **7** was not completely unexpected, since cyclopropanone **7** is severely destabilized by the steric repulsion of the eclipsed vicinal *t*-butyl groups. The magnitude of this unfavorable interaction is apparently large enough to completely reverse the ordinary position of equilibrium between the allene oxide-cyclopropanone pair. One of the few reactions that **5** has thus far been induced to undergo is the acid catalyzed isomerization to ketone **8**, a transformation that requires several days in the presence of boron trifluoride in refluxing ether to effect complete conversion. Compound **8** is very similar to one of the acid rearrangement products of 2,2-di-*t*-butylcyclopropanone (5), and its formation presumably involves ring-opened intermediate **9**.



The mass spectrum (70 eV) of **5** shows important fragments at *m/e* 224 (M^+), 154, 126, 111 (base), 97, 83, and 57. It is interesting that the *m/e* 126 fragment which has formally lost the elements of *t*-butylketene is common to the spectrum of 2,2-di-*t*-butylcyclopropanone (5). This observation raises the possibility that related open-chain ions (eg. **10**) intervene in the mass-spectral decomposition of these two species.

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REFERENCES

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