

CHEMISTRY OF SINGLET OXYGEN: ISOLATION AND CHARACTERIZATION OF A STABLE ALLENE OXIDE FROM A FULVENE ENDOPEROXIDE¹

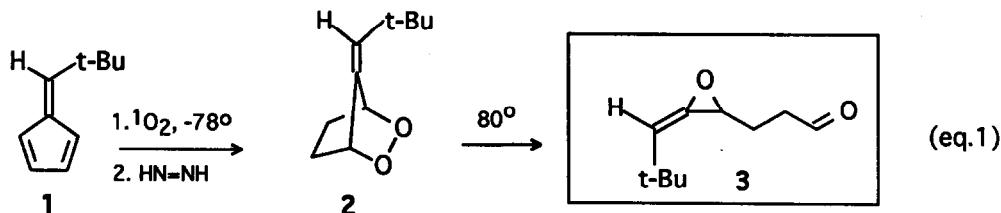
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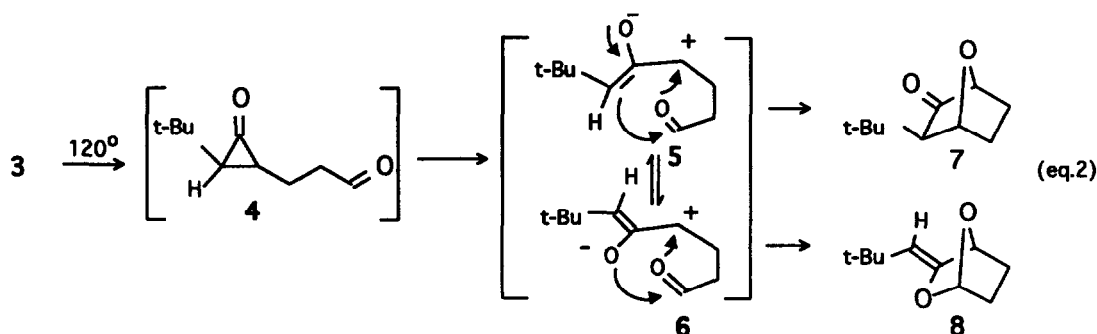
Abstract: Decomposition of the saturated endoperoxide derived from 6-*t*-butylfulvene at 100°C gives a stable allene oxide which was isolated and characterized by spectroscopy and chemical transformations. The thermal isomerization of the parent unsaturated system is also described and the decomposition mechanisms are discussed.

The photooxygenation of 6-substituted fulvenes has been one of the most intriguing reactions in singlet oxygen chemistry.²⁻⁶ The oxepinones isolated from these reactions have been ascribed to postulated allene oxide and/or cyclopropanone intermediates, *albeit* without corroborating evidence. Recently, our studies on the thermolysis of the saturated analogs have provided the first experimental evidence (as inferred from trapping reactions), that cyclopropanones indeed intervene as transient species in these reactions.⁷ In this communication we report the isolation and characterization of an allene oxide, which has been suggested as an intermediate, but which has hitherto eluded detection in the aforementioned endoperoxide rearrangements.

In view of the reported stability exhibited by epoxides derived from *t*-butyl allenes,⁸ we chose 6-*t*-butyl fulvene as our endoperoxide precursor. Photooxygenation of **1** at -78° in CH₂Cl₂ followed by diazene reduction^{9,10} at ~ -40° C gave the bicyclic peroxide **2** in 90% yield. Its ¹H NMR spectrum (CDCl₃, TMS) exhibits signals at δ 5.52 (s, 1H), 5.17 (s, 1H), 4.54 (s, 1H), 2.0 (m, 2H), 1.75 (m, 2H), 1.14 (s, 9H); ¹³C NMR (CDCl₃, TMS): δ 140.5, 128.2, 79.8, 74.3, 33.5, 30.6, 29.1, 28.9 ppm, consistent with the assigned structure. Thermolysis of this compound in CCl₄ at 80° C gave, almost exclusively,¹¹ a product which was isolated by vacuum distillation and purified by preparative TLC. Based on its spectral data it was identified as the allene oxide **3**. Its ¹H NMR spectrum displays signals at δ 9.79 (s,



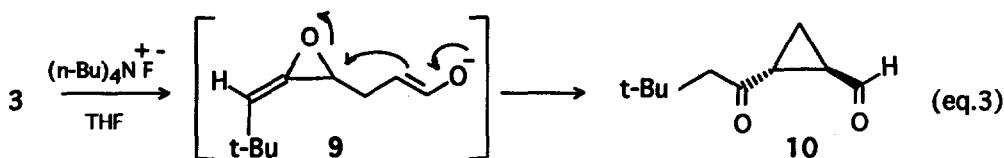
1H); 4.90 (s, 1H); 3.75 (dd, $J = 5.1, 3.0$ Hz, 1H); 2.45 (m, 2H); 1.90 (m, 2H); 1.1 (s, 9H). Its ^{13}C NMR spectrum contains 8 signals at δ 201.2, 135.7, 100.3, 60.0, 39.1, 31.4, 29.2, 24.2 ppm. The FT-IR spectrum (neat) shows characteristic absorptions at 2960, 2906, 2868, 2831, 2725, 1807, 1728, 1477, 1464, 1397, 1363, 1262, 1136, 1097, 1086, 1041, 1009 cm^{-1} . These spectra are remarkably similar to those reported for the 1,3-di-*t*-butylallene oxide^{8a} and entirely consistent with the structure of 3. This allene oxide is one of the very few stable analogs of its kind, and as in the previous cases it apparently owes its stability to the steric bulk of the *t*-butyl group on the double bond. Compound 3 also is the first of its kind bearing a functional group on the side chain. This compound proved to be quite stable thermally, and slowly decomposed at 120°C in CCl_4 in a sealed tube upon prolonged heating. The ^1H NMR spectrum taken of the crude thermolysis mixture showed the presence of two compounds which were isolated by preparative TLC and identified as 7 and the bicyclic acetal 8 based on their spectral data.¹² The latter compound is similar to the major thermolysis product obtained from the dimethyl



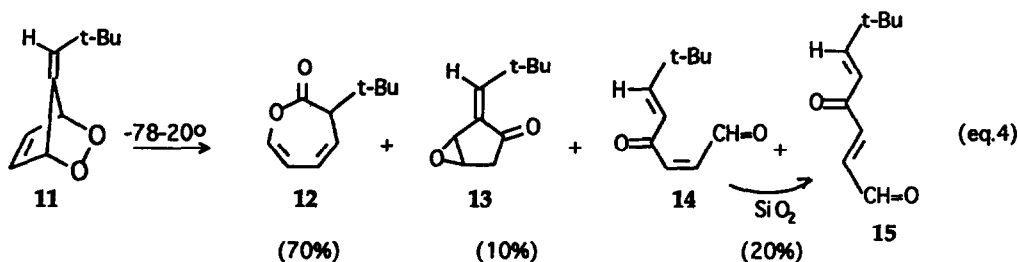
analog of 2, however, the 7-oxabicyclo[2.2.1]heptanone derivative 7 had not been observed in the previous case. Both 7 and 8 likely stem from intramolecular cycloaddition of the transient cyclopropanone to the aldehyde group in 4. Such 1,3-dipolar (intermolecular) cycloadditions of cyclopropanones to carbonyl compounds have previously involved combination of the C=O group with the cyclopropanone only across C2-C3, rather than O-C2 leading to cyclic acetals¹³ of the type 8. Ketone 7 in that regard is an unexpected product.

Additional proof for 3 was obtained by a chemical transformation reaction. It was speculated that nucleophilic attack on the epoxide carbon in 3 would result in ring cleavage giving an α -Nu (Nu= e.g., Cl^-) ketone, analogous to reactions of *in situ* generated allene oxides in the presence of halides.¹⁴ Instead, a completely different type of reaction was observed when 3 was treated with tetra-*n*-butylammonium fluoride in tetrahydrofuran: the 1,2-dicarbonyl substituted cyclopropane 10 was obtained. It was isolated by preparative TLC and characterized by its spectral data.¹⁵ The

formation of 10 is presumably initiated by enolate formation prior to intramolecular nucleophilic attack on the epoxide carbon.



Since the *t*-butyl group on the exocyclic double bond proved to exert a stabilizing effect on both the peroxide 2 and the allene oxide 3, it was hoped that the parent unsaturated system 11 might also give rise to an isolable allene oxide. However, photooxygenation of 6-*t*-butylfulvene in CH_2Cl_2 at -78°C and slow warm up to room temperature gave a mixture of 12, 13, 14 and 15 instead. These were separated from one another by preparative TLC and identified on the basis of their spectra.¹⁶ Oxepinones of the type 12 are principal products from thermal decomposition of all 7-substituted unsaturated fulvene endoperoxides.²⁻⁶ Products of the type 13 and 14/15, on the other hand, have never been observed in these reactions previously.¹⁷ Ketoaldehyde 14 quantitatively isomerizes to its *trans*-isomer 15 on SiO_2 .



The generation of allene oxides and cyclopropanones from saturated fulvene endoperoxides constitutes a novel entry into these unusual classes of compounds. Owing to the fact that the labile O-O bond in cyclic peroxides can be cleaved thermally as well as photochemically, one might isolate other less stable allene oxides from fulvene endoperoxides by photolysis at low temperatures. We are pursuing this latter aspect of the chemistry described herein.

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References and Notes

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11. Along with 3, small amounts of *t*-Bu-CH=CHC(O)CH₂CH₂CH=O was also formed; ¹H NMR (CDCl₃, TMS): δ 9.85 (s, 1H); 6.9 (d, 1H, J= 16.2 Hz); 6.05 (d, 1H, J= 16.2 Hz); 2.85 (m, 2H); 2.70 (m, 2H); 0.98 (s, 9H).
12. (a) 7: ¹H NMR (CDCl₃, TMS): δ 4.8 (dd, 1H, J= 4.8, 5.7 Hz); 4.36 (d, 1H, J= 6.4 Hz); 2.5 (d, 1H, H= 5.7 Hz); 1.5-2.0 (m, 4H); 1.05 (s, 9H); (b) 8: ¹H NMR (CDCl₃, TMS): δ 5.9 (s, 1H); 4.8 (dd, 1H); 4.2 (s, 1H); 1.6-1.9 (m, 4H); 1.07 (s, 9H).
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15. 10: ¹H NMR (CDCl₃, TMS): δ 9.35 (d, 1H, J= 4 Hz); 2.55 (m, 1H); 2.51 (s, 2H); 2.4 (m, 1H); 1.6 (m, 1H); 1.5 (m, 1H); 1.03 (s, 9H); ca. 10% *cis*-isomer was also present: δ(CH=O) 9.4 (d, J=3.6 Hz); ¹³C NMR (CDCl₃, TMS): δ 207.0, 199.0, 34.4, 31.1, 30.5, 27.6, 17.5; FT-IR (neat): 2960, 2871, 2731, 1715, 1696, 1466, 1384, 1368, 1321, 1196, 1154, 1096, 1023, 965.
16. Details of the spectra of 12, 13, 14 and 15 will be reserved to a forthcoming full report; 13 isomerizes to the corresponding unsaturated hydroxyketone upon prolonged storage in CDCl₃.
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