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A NOVEL THERMAL EPOXIDATION OF A
BICYCLO[3.1.0]HEX-2-ENE BY MOLECULAR OXYGEN

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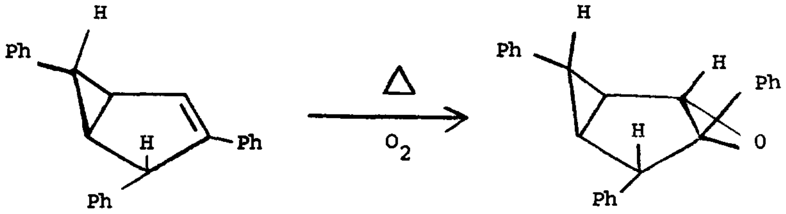
As an extension of our studies on the photochemical Diels-Alder reaction of 1,3,5-hexatrienes to bicyclo[3.1.0]hex-2-enes,[1] we became interested in determining the stereochemical consequences attending the thermal cycloreversion of the bicyclo[3.1.0]hex-2-ene system. The parent carbocycle is known to display interesting thermal chemistry. At 255° it undergoes a degenerate vinylcyclopropane rearrangement[2] and at higher temperatures it isomerizes to a mixture of 1,3- and 1,4-cyclohexadienes.[3] An allylically stabilized diradical has been postulated as an intermediate in these reactions.[3,4] Some recent work in the literature suggests however, that the thermal rearrangements of bicyclo-[3.1.0]hex-2-enes with electron-withdrawing substitutents at the 6 position may be proceeding through a 2 + 4 cycloreversion.[5-7] The constraints imposed upon such a reaction by orbital symmetry factors makes it of more than usual mechanistic interest. If the thermal reversion of the bicyclo[3.1.0]hex-2-ene system is to be concerted, the process necessarily must take place *via* the $\pi 4s + \pi 2s$ pathway.[8] Our initial attempts to uncover an example of such a process led us to examine the thermal behavior of the 3,4,6-triphenylbicyclo-[3.1.0]hex-2-ene system. In this communication we describe a novel epoxidation reaction which results when the bicyclohexene system is heated in an inert solvent in the presence of oxygen.

When a xylene solution of exo,exo-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (**1**) was heated at reflux, starting material was observed to be transformed gradually into a single product (76% yield after 48 hr); significant polymer formation was also noted. Preparative thick layer chromatography of the crude reaction mixture gave a colorless solid, mp 118-119°, which was identified as exo,exo-2,3-epoxy-3,4,6-triphenylbicyclo[3.1.0]hexane (**2**) on the basis of its spectral properties,[9] particularly its unequivocal nmr spectrum: λ_{max}^{KBr} 6.23, 6.69, 6.90, 9.50, 10.78, and 11.10μ; λ_{max} (cyclohexane) 265 nm (ε 1300):

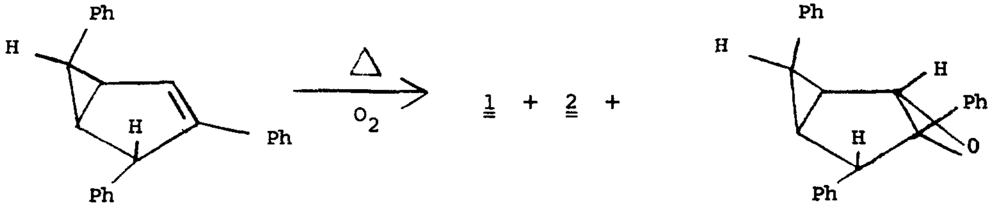
m/e 324; $\delta_{TMS}^{CDCl_3}$ 1.66 (*m*, 1H, C_1H), 2.05 (*t*, J = 3.0 Hz, 1H, C_5H), 2.38 (double *d*, J = 6.0 and 3.0 Hz, 1H, C_6H), 3.78 (*s*, 1H, C_4H), 4.06 (*s*, 1H, C_2H) and 2.7 (*m*, 15H, aromatic). Final confirmation of structure **2** was achieved by direct comparison with an authentic sample prepared by the peracid epoxidation of **1**.



1 **2**

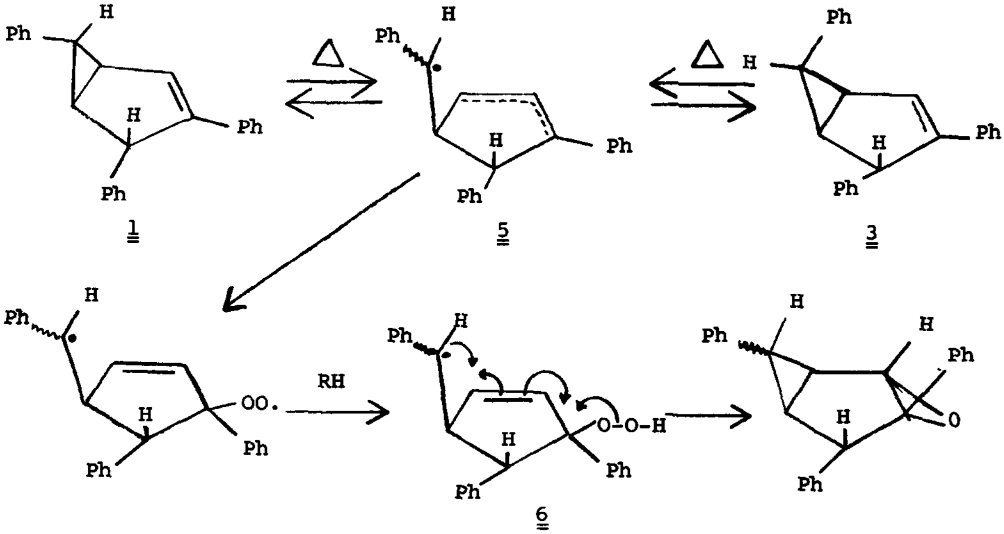
Lanthanide-induced differential shifting of the nmr spectrum of **2** using $Eu(fod)_3$ served to indicate that the epoxide group was located anti to the cyclopropyl ring.

To elucidate the mechanism responsible for the formation of **2**, the thermolysis of the corresponding *exo,endo*-bicyclo[3.1.0]hex-2-ene **3** was examined. Heating a solution of **3** in mesitylene for 40 hr gave rise to a mixture of three products **1**, **2**, and **4** in a ratio of 2:2:1. Spectral data[9] on a purified sample of **4**, mp 81-83°, suggested that it was *exo,endo*-2,3-epoxy-3,4,6-triphenylbicyclo[3.1.0]hexane; λ_{max}^{KBr} 6.23, 6.70, 6.91, 7.12, 9.25, 10.60, 10.96μ; λ_{max} (cyclohexane) 265 nm (ε 1200); m/e 324; $\delta_{TMS}^{CDCl_3}$ 1.70 (*t*, 1H, J = 7.0 Hz), 2.45 (*t*, 1H, J = 7.0 Hz); 2.52 (*t*, 1H, J = 8.0 Hz); 3.50 (*s*, 1H), 3.59 (*s*, 1H), 6.2-6.3 (*m*, 2H), 6.9-7.4 (*m*, 13H). Corroborative evidence for this formulation was derived by epoxidation of **3** with *m*-chloroperbenzoic acid.



3 **4**

Thermolysis of either **1** or **3** at 160° under a nitrogen atmosphere yielded the same equilibrium mixture of the two bicyclohexenes **1** and **3** (ratio 16/1). The transformation leading to epimerization of the bridge substituents can be formally depicted as proceeding *via* cleavage of the external cyclopropane ring. Several examples of thermal and photochemical epimerizations in systems similar to **1** have recently been reported[10-13] and provide good chemical analogy for the observed isomerization. A rationale that explains the epoxidation results and is also consistent with the thermal epimerization is based on the assumption that the diradical intermediate **5** reacts with oxygen to give a peroxide radical **6** which undergoes subsequent intramolecular radical displacement.



The above reaction scheme is somewhat related to the sequence of steps involved in cyclic ether formation during vapor phase hydrocarbon oxidation.[13-17] The solvent system employed is most important since the epoxidation reaction failed when the thermolysis was carried out in tetrachloroethylene. This would imply that the peroxy radical must abstract a hydrogen from the solvent in order for the epoxide to be formed.

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