274. Propellanes

Part LXXII

The Structure of the 4-Methyl-1,2,4-triazoline-3,5-dione Adduct of the Propellane Lactone Obtained by Oxidation of Biphenylene[1]

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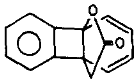
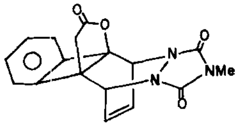
Summary

The title compound reacts with the dienophile by attacking the face of a cyclohexadiene ring which is *syn*- to the lactone ring.

Kurosawa & McOmie [2] have reported a number of oxidation products obtained from biphenylene by treatment with manganous (III) acetate in refluxing acetic anhydride. One of these was a propellane lactone **1**.



1



2

Although we have submitted a propellane lactone to *Diels-Alder* reactions with triazolinediones, the positions of the carbonyl and ether O-atoms in such a substrate were reversed [3] with respect to **1**. A mixture of products resulted in which the cyclohexadiene face was attacked from both the *syn*- and the *anti*-side with respect to the lactone ring. On the other hand, in a cyclic carbonate (similar to **1** but for one ether O-atom being formally replaced in **1** by a CH_2-group) attack by the dienophile was solely from the *anti*-face [4].

Usually we have found that when cyclobutene or cyclobutane occur in a propellane with larger rings, a cyclohexadiene ring in the propellane is attacked exclusively *anti* to these four-membered rings [5], as would be expected for a benzo-substituted-cyclobutene.

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[1] Part LXXI: [1].

Thus **1** should be attacked at the cyclohexadiene face *anti-* to the benzocyclobutene moiety, *i.e. syn* to the lactone ring. The structure of **2** was shown by X-ray crystallography [6] to be as shown in **2** and its ORTEP projection *(Figure)*. The 4-methyl-1,2,4-triazoline-3,5-dione indeed enters *syn* to the lactone ring, *anti* to the benzocyclobutene moiety.

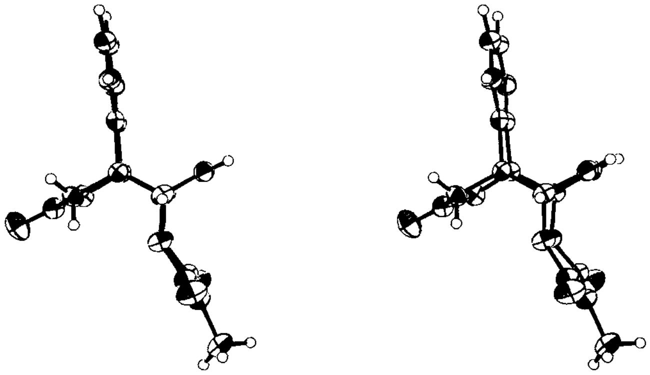

Figure. *ORTEP Projective of* **2**

We thank Dr. *McOmie* for sending us a sample of **1** prepared by Dr. *Kurosawa*.

Experimental. – To a CH_2Cl_2 (5 ml) solution of **1** (52 mg) was added a CH_2Cl_2 solution (3 ml) of MTAD (28 mg). Reaction was instantaneous as shown by immediate disappearance of the red color of the dienophile. Removal of solvent afforded after crystallization a colorless product **2** (63 mg), m.p. 239–240° (benzene/hexane). IR ($CHCl_3$): 1780, 1710, 1460, 1400. ^{1}H-NMR ($CDCl_3$): 7.45–7.20 (*m*, 4 H, C_6H_4); 6.10 (*m*, 2 vinylic H); 5.40 (*m*, 1 H, CHN); 5.20 (*m*, 1 H, CHN); 3.08 (*s*, 2 H, CH_2CO); 3.03 (*s*, 3 H, NCH_3). MS: 323 (50); 209 (31.6); 181 (100); 165 (17.5); 153 (28). M.w.: Calc. 323.0916, Found 323.0899.

$C_{12}H_{13}N_3O_4$ Calc. N, 13.00%. Found N 12.75%.

The crystals for X-ray analysis were obtained from ethyl acetate.

REFERENCES

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