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PROPELLANES. PART LXXXV.[†]

CONFIRMATION OF PREDICTED REGIOSPECIFICITY IN DIELS-ALDER REACTIONS OF CERTAIN PROPELLANES WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE

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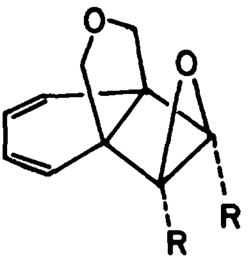
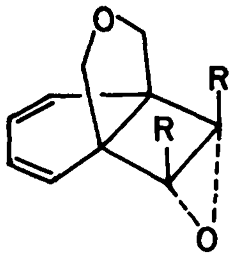
Abstract.- PTAD attacks 1b and 2b from the side of the five-membered ether ring, i.e. anti- to the substituted cyclobutane ring.

We predicted correctly that both the propellanes 1a and 2a[1] would react with PTAD exclusively





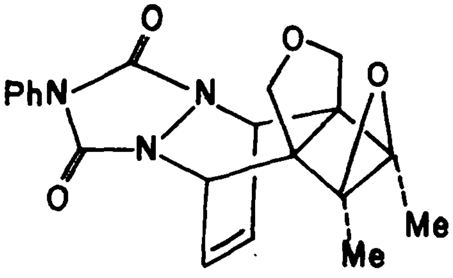
1 a R=H 2 a
1 b R=Me 2 b

at the face of the cyclohexadiene which is syn- with respect to the 5-membered ether ring, for steric repulsion to attack at the anti-face would be greater whether hydrogen atoms or the epoxide oxygen (in which electrostatic repulsion can also play a role) are present as substituents in the cyclobutane ring[2].

Clearly, the same should hold for 1b and 2b in which even larger methyl groups are present instead of the cyclobutane hydrogens. We thus made the same prediction for direction of attack by the same dienophile[2] and we have now put this to the test.

Pure samples of the PTAD adducts of 1b and 2b were prepared and subjected to X-ray analysis. That from 1b from gave 3 (prisms) of structure 3 (see ORTEP of 3) whilst that from 2b gave 4 (needles) (see ORTEP of 4).

[†] Part LXXXIV: P. Ashkenazi, O. Weinberg, Andrei Zlota, and D. Ginsburg, *Synthesis*, in press.



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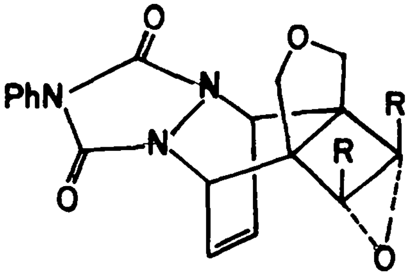

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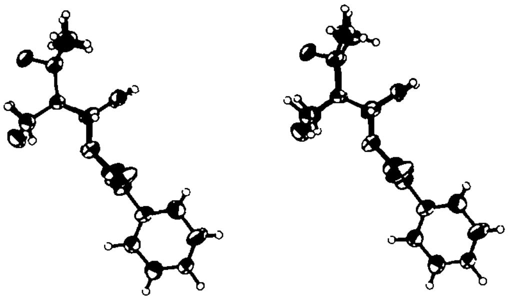
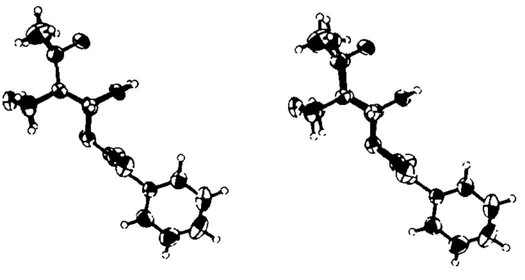
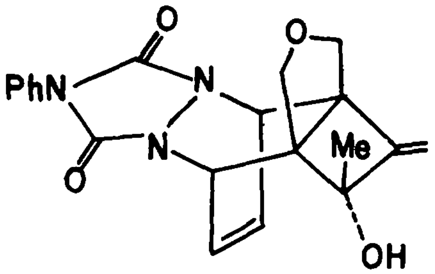


ORTEP of 3

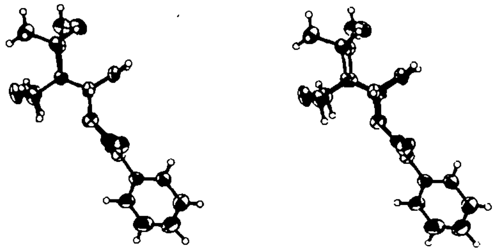


ORTEP of 4

We also had at our disposal a decomposed sample of 2b (epoxide ring anti to 5-membered ether ring) which contained several products. Upon reaction with PTAD, three fractions could be isolated by TLC, fine needles and an amorphous solid both unsatisfactory for X-ray analysis and yellowish needles which were analyzed and proved to be 5, a member of the 4 (or 2b) family. It had its one remaining methyl group syn to the ether ring, one hydroxyl anti to it, and a methylene group in the plane of the cyclobutane ring.



5



ORTEP of 5

Although we can write a mechanism of formation of 5 we desist since we did no work to support it.

Corrigendum - One of us (G.M.) has strenuously objected to the (mistaken) insertion (at the writing-table stage) of footnote 2 on p. 2710 in Ref. 2 but politely accommodated the inferior judgment of D.G. The point involved has been rechecked. We must now delete that footnote. The change mentioned is *not* required in Ref. 1. However, although the ORTEP drawings in Ref. 2 are correct for 2a and 2b, these numbers must be reversed in the experimental section, p. 2710 in

Ref. 2. In the experimental work on the present paper 1b and 2b were carefully kept separate so as to avoid any recurring error of the above type.

EXPERIMENTAL PART

Compound 3 was purified on a preparative silica plate using $CHCl_3$ as eluent, m.p. 274-278° ($CHCl_3$/hexane). IR($CHCl_3$): 1780, 1720, 1410, 1260. ^1H-NMR ($CDCl_3$): 7.2 (s, 5 aromatic); 6.45 (t, 2 vinylic); 4.9 (t, 2 vinylic); 4.9 (t, 2 CHN); 3.8 (s, 4 CH_2O); 1.25 (s, 6 CH_3). MS: 365 (19 M^+), 269 (81), 227 (100), 188 (15), 177 (5), 128 (5). M.W.: calc. 365.1375 found 365.1371.

Compound 4 was similarly purified using AcOEt/CH_2Cl_2 1:4, m.p. 232-233° (CH_2Cl_2/hexane). IR: 1780, 1720, 1410, 1260. ^1H-NMR ($CDCl_3$): 7.2 (s, 5 aromatic); 6.35 (t, 2 vinylic); 4.9 (t, 2 CHN); 4.0 (s, 4 CH_2O); 1.4 (s, 6 CH_3). MS: 365 (10 M^+), 269(38), 227 (100), 188 (11), 177 (3), 159 (17). M.W.: found 365.1383.

Compound 5 was similarly purified, using $CHCl_3$. IR ($CHCl_3$): 1780, 1720. ^1H-NMR ($CDCl_3$): 7.2 (s, 5 aromatic); 6.4 (m, 4 vinylic); 5.1, 4.85 (m, 2 CHN); 3.9 (s, 4 CH_2O); 1.4 (s, 3 CH_3). MS: 365 (96, M^+), 227 (50), 190 (14), 188 (18), 177 (26), 175 (16), 172 (12), 159 (100), 147(46), 145 (5), 138 (9). M.W.: found 365.1371.

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1. G. Maier, T. Sayraç, and H.P. Reisenauer, *Chem. Ber.*, *115*, 2202 (1982).

2. P. Ashkenazi, M. Kaftory, T. Sayraç, G. Maier, and D. Ginsburg, *Helv. Chim. Acta*, *66*, 2709 (1983).