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PROPELLANES—XXXI

THE DIELS–ALDER REACTION OF [4.4.2]PROPELLANES WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE[a]

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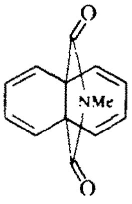
Abstract—Attack of a number of [4.4.2]propellanes by the dienophile named in the title occurs, when one equivalent of dienophile is used, from the direction *anti*- to the 4-membered ring.

IT HAS been claimed that secondary orbital interactions are responsible for the exclusive attack of **1** by **2** from "above" (*syn*- to the heterocyclic ring).[1-3] Thus, it may appear at first sight that the [4.4.2]propellatetraene **3** would also be attacked from the same direction as the *p*-orbitals of the cyclobutene double bond would have apparent capability for effective overlap with the lone pair orbitals of **2** in analogy to that apparently exerted by the corresponding carbonyl orbitals of **1**.



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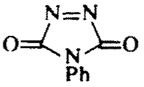

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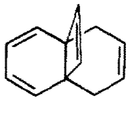

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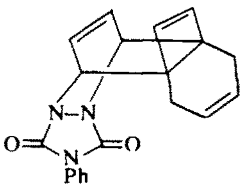

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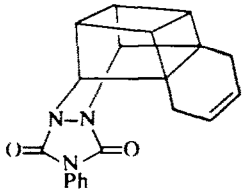

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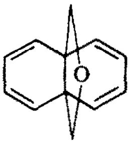
The fact that **2** attacks **3** exclusively from below to afford **4**[4] appeared to weaken our argument in the case of **1**. Since irradiation of **4** afforded **5** it is unequivocally proved that attack had indeed occurred from below.

In the case of the ether **6** we explained exclusive attack from below by invoking steric hindrance exerted by the hydrogens adjacent to the ether oxygen to attack from above.[1-3] Thus, we would have predicted by analogy that [4.4.2]propellanes containing a cyclobutane ring would also be attacked from below, e.g. **7**. The steric course of reaction could easily be proved by correlation with **4** of known configuration, serving as the frame of reference.



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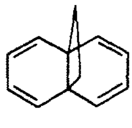

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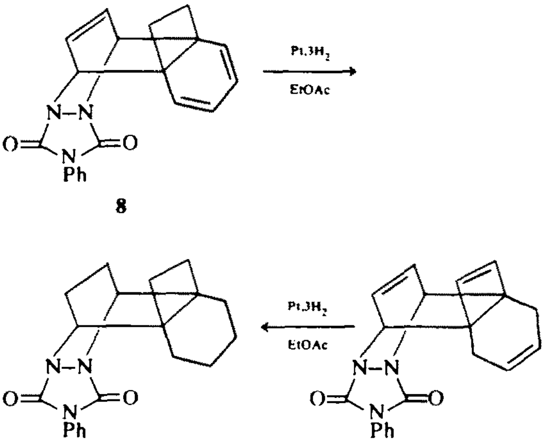
Thus, it was not surprising that both **8**, the mono-Diels–Alder adduct of **7**, and **4**, when reduced to the corresponding perhydro-derivative, gave the identical substance, **9**.



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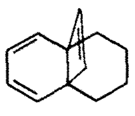
9 **4**

Incidentally, **7** gave an unsymmetrical *bis*-adduct as evidenced by the AB quartet exhibited by the cyclobutane protons in **10**. This is entirely analogous to the behavior of **6** which also gives an unsymmetrical *bis*-adduct on reaction with **2**. Two additional substrates **11** and **12** were available, with a cyclobutene[5] and a



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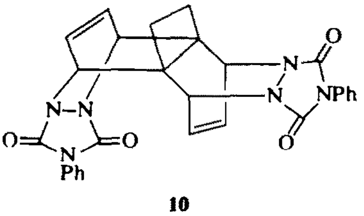

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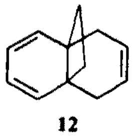

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[a] Propellanes. XXX. A. Rüttimann and D. Ginsburg, *Angew. Chem.* in press.

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cyclobutane ring,[6] respectively. Both were attacked by **2** exclusively from below as evidenced by reduction of the respective adducts **13** and **14** to the same perhydrocompound **9**.

The H atoms attached to the cyclobutene double bond in **4** or in **11** clearly do not exert steric hindrance towards attacks from above to the degree exerted by the cyclobutane hydrogens in **8** and in **12**. It is also clear that the cyclobutene *p*-orbitals do not act to reverse the direction of attack in the saturated cases. Professor R. Gleiter has performed calculations of the orbital energies concerned in interaction with the pertinent lone pair orbitals of **2** and finds that those of the *p*-orbitals in the cyclobutenes are too high in energy for effective overlap to occur.[7] These and results of other calculations will be reported elsewhere. Thus, no assistance for attack from above, *syn* to the cyclobutene ring, comes from this quarter.

EXPERIMENTAL

Preparation of bis-adduct **10**. To a soln of **7**[8] (52 mg) in CH_2Cl_2 (3 ml) was added dropwise with magnetic stirring a solution of **2** (117 mg) in the same solvent (3 ml). After removal of solvent, crude **10** was obtained quantitatively. The analytical sample formed colorless crystals, m.p. 273–275° (hexane-CH_2Cl_2). (Found: C, 66.25; H, 4.34; N, 16.47; M.W. 506.1760. $C_{28}H_{22}N_6O_4$ requires: C, 66.39; H, 4.38; N, 16.59%; M.W. 506.1702). IR ($CHCl_3$): 1770, 1715 cm^{-1} (CO). NMR ($CDCl_3$): τ 2.42 (s, 5 arom H); 2.47 (s, 5 arom H); 3.20 (t, J = 3 Hz, 2 vinylic H); 3.52 (t, J = 3 Hz, 2 vinylic H); 4.90 (t, J = 3 Hz, 2 allylic H); 5.07 (t, J = 3 Hz, 2 allylic H); 7.27–7.53 (m, 2 cyclobutane H); 8.17–8.50 (m, 2cyclobutane H).

Preparation of monoadduct **8**. Reaction of **7** (52 mg) in CH_2Cl_2 (3 ml) with **2** (58.3 mg) in CH_2Cl_2 (3 ml) as above afforded **8** (95%) as colorless crystals, m.p. 207–208° (benzene-hexane). (Found: M.W. 331.1292. $C_{20}H_{17}N_3O_2$ requires; 331.1320). IR ($CHCl_3$): 1770, 1710 cm^{-1} (CO). NMR ($CDCl_3$): τ 2.50 (s, 5 arom H); 3.15 (t, J = 3 Hz, 2 vinylic H); 3.77–4.50 (m, 4 H, conjug diene); 5.27 (t, J = 3 Hz, 2 allylic H); 7.50–8.34 (m, 4 H, cyclobutane H).

Preparation of monoadduct **13**. A soln of **11**[5] (53 mg) in CH_2Cl_2 (3 ml) was treated with a solution of **2** (58.3 mg) in CH_2Cl_2 (3 ml). The product formed colorless crystals (80 mg; 72%), m.p. 229–231° (dec, benzene-hexane). (Found: M.W. 333.1459. $C_{20}H_{19}N_3O_2$ requires: 333.1477). IR ($CHCl_3$): 1790, 1725 cm^{-1} (CO). NMR ($CDCl_3$): τ 2.49 (s, 5 arom H); 3.77 (t, J = 3 Hz, 2 vinylic H); 4.03 (s, 2 cyclobutene H); 5.37 (t, J = 3 Hz, 2 allylic H); 7.67–8,67 (m, 8 $C\underline{H}_2$).

Preparation of monoadduct **14**. A soln of **12**[6] (53 mg) in CH_2Cl_2 (3 ml) was treated with a soln of **2** (58.3 mg) in the same solvent (3 ml) and worked up as above, affording **14** as colorless crystals (80%), m.p. 201–203° (dec, benzene-hexane). (Found: M.W. 333.1493. $C_{20}H_{19}N_3O_2$ requires: 333.1477). IR ($CHCl_3$); 1760, 1710 cm^{-1} (CO). NMR ($CDCl_3$): τ 2.50 (s, 5 arom H), 3.30 (t, J = 3 Hz, 2 vinylic H); 3.72–3.93 (m, 2 vinylic H); 5.43 (t, J = 3 Hz, 2 allylic H); 7.34–7.92 (m, 4 allylic H); 8.43 (s, 4 cyclobutane H).

Reduction procedure. A soln of monoadduct (30 mg) in EtOAc (20 ml) was shaken for 8 hr in presence of Pd/C (10%; 10 mg) and H_2 (1 atm). Catalyst and solvent were removed and the product was crystallized to constant m.p.

Reduction of **4**[4] afforded the authentic specimen of the perhydro-derivative **9** as colorless crystals, m.p. 174–175° (benzene-hexane). (Found: M.W. 337.1790. $C_{20}H_{23}N_3O_2$ requires: 337.1790). Ir ($CHCl_3$): 2950, 2850 (CH); 1755, 1690 (CO); 1600, 1400, 1135 cm^{-1}. NMR ($CDCl_3$): τ 2.23–2.80 (m, arom H), 6.03 (s, 2 $C\underline{H}N$); 7.20–7.87 (m, 4 $C\underline{H}_2$); 8.00 (s, 4 cyclobutane H); 8.03–8.73 (m, 8 $C\underline{H}_2$).

Reduction of **8** afforded the perhydro-derivative, m.p. 173–174° (benzene–hexane), m.m.p. with authentic **9**, 174–175°; IR spectra superimposable.

Reduction of **13** afforded **9**, m.p. 174–175°, m.m.p. 174–175°; IR spectra superimposable.

Reduction of **14** required, after isolation of crude product, chromatography on a silica plate (20 × 20 cm) using acetone-hexane (1 : 3) and extraction with EtOAc. Removal of solvent and crystallization gave **9**, m.p. 172–173°, m.m.p. with authentic **9**, 173–174°; IR spectra superimposable.

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