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PROPELLANES—XLI

THE DIELS–ALDER REACTION OF A TETRAENIC LACTONE WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE†

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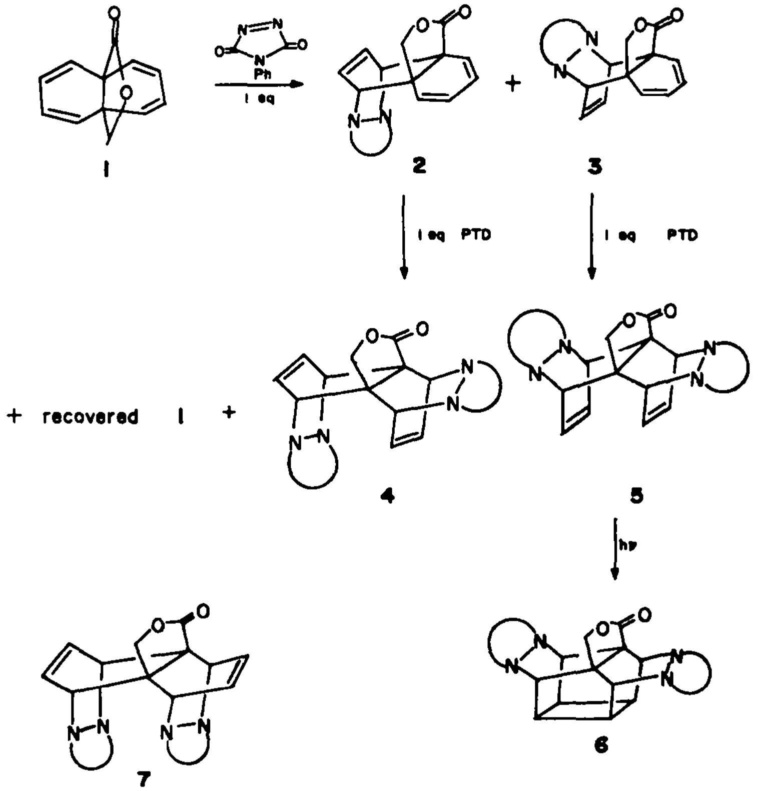
Abstract—The tetraenic lactone **1** affords the two configurationally possible mono-Diels–Alder adducts. Each of these afforded a *bis*-adduct. The configurations of all of these adducts have been established.

In continuation of our studies on the steric course of the Diels–Alder reaction in many propellane substrates[1] we have used the tetraenic lactone **1**.[2] Such a compound is structurally unable to emulate the related anhydride or imides in secondary orbital interaction with the pertinent orbitals of the azo-nitrogens in the dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) so as to undergo attack exclusively from the top face.[1]

Thus it is not surprising that instead of a single Diels–Alder 1:1 adduct, a more complex reaction mixture was obtained. In addition to the two configurationally possible mono-adducts **2** and **3**, some *bis*-adduct **4** was also formed and, hence, some unreacted starting material was also recovered. Scheme 1 summarizes the course of this reaction. Also shown in this scheme is the structural proof for the various configurations assigned to the



Scheme 1.

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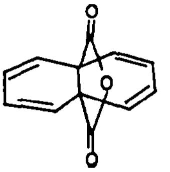
†Part XL: K. Bachmann, W. von Philipsborn, C. Amith and D. Ginsburg, *Helv. Chim. Acta* **60**, 400 (1977).

above products. The mono-adduct 2 after isolation and purification was treated with a second equivalent of the dienophile, again affording the same *bis*-adduct 4 which accompanied the two mono-adducts in the original reaction mixture.

Since pure 3 afforded an isomeric *bis*-adduct 5 which upon irradiation gave in turn the cage compound 6, the various configurations follow logically and of necessity.

The argument is a simple one: Only 5 may undergo a [2 + 2] photocycloaddition. Since both equivalents of dienophile must have attacked from above in order to afford 5, the first equivalent of PTD must also have attacked from above, i.e. the mono-adduct which afforded 5 *must* have been 3. Since symmetry tells us that there can only be *two* isomeric mono-adducts, 2 and 3, the isomer of 3 isolated from the product mixture *must* have been 2. Whilst 2 may, in principle, afford another *bis*-adduct 7, we known by experience that the second equivalent of dienophile usually attacks from above for steric reasons,[1] with the notable exception of bridged[10] annulenes.[3] We have no reason to believe that the lactone ring for either steric or electronic reasons should guide the second equivalent of PTD to the bottom face, particularly when we have proved that 9 affords the *bis*-adduct analogous to 4, *not* to 7.

It is not surprising that the mixture containing both 2 and 3 is obtained rather than only one of these as an exclusive reaction product. If we compare the transition state leading to 3 with that of the corresponding anhydride 8 we do not obtain in the former case analogously effective secondary orbital overlap. The two hydrogen atoms in the CH_2 group of the lactone ring evidently exert steric hindrance to approach of the dienophile from the top face, sufficiently to cause the formation of 2. That 2 does not form exclusively as in the case of the ether 9 appears to mean that some secondary orbital overlap does indeed occur between the CO group in the lactone ring and the lone pair of one of the azo nitrogen atoms of PTD.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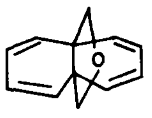
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EXPERIMENTAL

IR spectra were measured on a Perkin–Elmer model 257 grating spectrometer. NMR spectra were measured on a Varian T-60 spectrometer. Mass spectra were measured on a Varian 711 spectrometer using the heated inlet system at 200°, maintaining the electron energy at 100 eV. Only the major fragments are listed. All m.ps are uncorrected.

Diels–Alder reaction of 1. A soln of PTD (254 mg) in CH_2Cl_2 chloride (4 ml) was added at once to one of 1 (270 mg) in CH_2Cl_2 (4 ml) at room temp. The red color disappeared immediately. Removal of solvent in a vacuum afforded the crude product (524 mg). After trituation with boiling benzene and removal of solid material (224 mg) by filtration (see below), the material in the filtrate (300 mg) was separated on 3 plates (20 × 20 cm) of silica gel (60 PF_{254} Merck) using acetone (1): hexane (1). From the top band 1 was recovered (65 mg; 16%). A mixture of 2 and 3 was obtained from the central band (150 mg) and a mixture (40 mg) was obtained from the bottom band.

The mixture of 2 and 3 was subjected to crystallization from benzene. Only isomer 2 dissolves and crystallizes upon addition of a little hexane (83 mg; 21%), m.p. 159–161° (benzene-hexane). (Found: C, 65.77; H, 4.22; N, 11.32. $C_{20}H_{15}N_3O_4$ requires: C, 66.47; H, 4.18; N, 11.32%). IR (KBr): 3060, 1770, 1710, 1510, 1415 cm^{-1}. NMR ($CDCl_3$): τ 2.53 (s, 5 arom H); 3.26 (t, J = 3 Hz, 2 vinylic H); 3.44–4.34 (m, 4 diene H); 4.77–5.17 (m, $2C\underline{H}N$); 5.80 (s, $2C\underline{H}_2OCO$). MS: 227 ($M^+-C_8H_6O_2$; 100); 134 (64); 119 (43).

Isomer 3 which was insoluble in benzene was obtained by filtration and was crystallized from chloroform (67 mg at this stage), m.p. 241–243° (dec, $CHCl_3$). (Found: C, 65.87; H, 4.12; N, 11.32%). IR (KBr): 3000, 2920, 1760, 1710, 1500, 1415 cm^{-1}. NMR ($CDCl_3$): τ 2.57 (s, 5 arom H); 3.36 (t, J = 3 Hz, 2 vinylic H); 3.80–4.34 (m, 4 diene H); 4.80–5.00 (m, $2C\underline{H}N$); 5.10, 5.73 (ABq, J = 10 Hz, 2 $C\underline{H}_2OCO$). MS: 227 (100); 134 (13); 119 (47).

The solid which did not dissolve during the first trituation with benzene (224 mg) was triturated first with chloroform, then with $CHCl_3$ (1): MeOH (1), affording insoluble (85 mg) *bis*-adduct 4 (see below). To the filtrate was added the material isolated from the bottom band of the silica gel plates (40 mg) and the whole was again separated on 3 silica gel plates using acetone (1): hexane (2). More of 4 was isolated (57 mg; total yield 35%), as well as more of 3 (56 mg; total yield 28%). Yields were calculated on the basis of the total material *isolated* (404 mg).

The *bis*-adduct 4 had m.p. 348–350° (dec). (Found: M.W. 536.1423. $C_{28}H_{20}N_6O_6$ requires: M.W. 536.1446). IR (KBr): 3060, 3000, 1770, 1715, 1500, 1410 cm^{-1}. NMR (DMSO-d_6): τ 2.43 (s, 10 arom H); 3.00–3.20 (m, 2 vinylic H); 3.36–3.50 (m, 2 vinylic H); 4.34–4.80 (m, $4C\underline{H}N$); 5.34, 5.80 (ABq, J = 10 Hz, $2C\underline{H}_2OCO$). MS: M^+, 536 (8); 292 (100); 227 (90); 119 (60).

Reaction of 2 with PTD. The mono-adduct 2 (36 mg) in CH_2Cl_2 (2 ml) was treated with a solution of PTD (17 mg) in CH_2Cl_2 (2 ml). The reaction was over in 3 min. The *bis*-adduct 4 was isolated in quantitative yield, identical in all respects with 4 described above.

Reaction of 3 *with PTD.* A soln of 3 (36 mg) in CH_2Cl_2 (2 ml) was mixed with one of PTD (17 mg) in CH_2Cl_2 (2 ml). The red color was discharged after the whole was allowed to stand overnight at room temp. Removal of solvent and trituration of the solid with MeOH afforded the *bis*-adduct 5 (45 mg; 85%), m.p. >350°. IR (KBr): 3060, 2920, 1760, 1720, 1500, 1400 cm^{-1}. NMR (DMSO-d_6): τ 2.43 (br s, 10 arom H); 3.20–3.80 (m, 4 vinylic H); 4.47–4.70 (m, 4 $C\underline{H}N$); 5.06 (br s, 2 $C\underline{H}_2OCO$). MS: $M^+-C_{16}H_{11}N_3O_4$, 227 (25); 134 (20); 119 (100).

Irradiation of 5. A degassed soln of 5 (30 mg) in acetone (50 ml) was irradiated for 18 hr at room temp. in a Rayonet apparatus using 3000 Å lamps. Removal of solvent and trituration with $CHCl_3$ afforded the cage product 6 quantitatively, m.p. >350°. (Found: M.W. 536.1445. $C_{28}H_{20}N_6O_6$ requires: M.W. 536.1446). IR (KBr): 2980, 1770, 1710, 1500, 1410 cm^{-1}. NMR (DMSO-d_6): τ 2.42 (br s, 10 arom H); 4.90 (br s, 2 $C\underline{H}_2OCO$); 5.00–5.25 (m, 4 $C\underline{H}N$); 6.70 (br s, 4 cyclobutyl H, observed only after adding TFA). MS: M^+, 536 (24); 227 (100); 119 (30).

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