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PROPELLANES—XLV

SYMMETRY CORRELATION OF DIELS–ALDER ADDUCTS OF TETRAENIC PROPELLANES WITH THEIR NMR SPECTRA[a]

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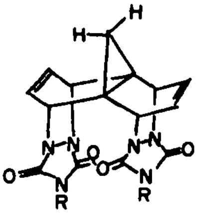
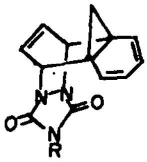
Abstract—Propellane derivatives having different symmetry have been prepared and their NMR spectra measured.

In a recent investigation of *bis*-Diel–Alder adducts which may formally be considered as derived from the [4.4.1] propellatetraene system the symmetry of the *bis*-adducts using 1,6-methano [10] annulene and 2 moles of either 4-methyl **3a** or 4-phenyl-1,2,4-triazoline-3,5-dione **3b** could be directly deduced by observing the singlet nature of the cyclopropyl protons in each of these adducts (**1a, b**).[1] However, the fact that the mono-adduct **2a** with the 4-phenyl-dienophile gives the same product, **1c**, as is obtained by treating the mono-adduct **2b** with the 4-methyl-dienophile, proves that **1c** has the same configuration as **1a** and **1b**.[1] The heterocyclic (4.4.3] propellatetraenes **4** and **5**, however, lead to products having different configuration. Compound **4** gives mainly a *bis*-adduct **6** of C_{2v} symmetry (the same symmetry as **1a, b**, albeit of different configuration) accompanied by a minor isomer of C_s symmetry.[2,3] The ether **5** gives exclusively the *bis*-adduct **7** of C_s symmetry.[2] In the latter case, it matters, of course, whether one reacts the mono-adduct **8a** with **3b** or **8b** with **3a**; chemically different di-adducts **7c** and **7d**, respectively, are obtained.



1a: R = Me
b: R = Ph



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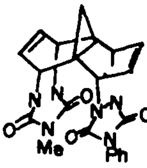
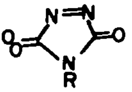


1c:



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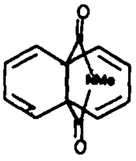

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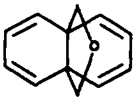

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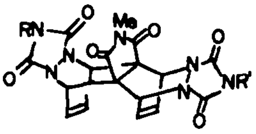
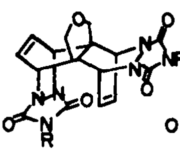
We were interested in gauging via NMR spectroscopy, the degree of discernment by various protons in the above compounds of their relatively more remote environments. The data is tabulated in the experimental section and it may be seen that although, for example, compounds of type **7** all exhibit an AB quartet for the $C\underline{H}_2O$ protons, thus distinguishing between a proximate double bond and a heterocyclic ring, in **6c** one finds only a single triplet for the vinylic protons and a single triplet for the $C\underline{H}N$ protons although there is a difference between the N–Me and N–Ph environment of two potential triplets, in each case.

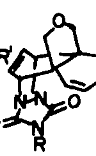
We prepared the diaza [4.3.3] propellane **10** and the dioxa analog **11**, and dithia [4.3.3] propellane **12** of C_{2v} symmetry, in order to observe similar details in the latter's NMR spectrum as compared to the oxa-thia [4.3.3] propellane **13** and its corresponding sulfone **14** (also of C_s symmetry). But in addition we wanted to find whether or not **13** and **14** direct the entry of the dienophile in the identical way or in the opposite way. Since **15**, the adduct of **13**, was oxidized to **16**, the adduct of **14**,



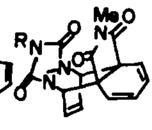
6a: R = R′ = Me
b: R = R′ = Ph
c: R = Me, R′ = Ph



7a: R = R′ = Me
b: R = R′ = Ph
c: R = Me, R′ = Ph
d: R = Ph, R′ = Me



8a: R = Me
b: R = Ph



9a: R = Me
b: R = Ph

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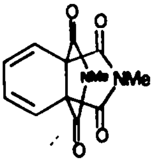
[a] Part XLIV. P. Ashkenazi, E. Vogel and D. Ginsburg, *Tetrahedron* 34, 2167 (1978).

it is clear that in both cases the dienophile enters from the same direction but we do not know whether this is *syn*- or *anti*- to the oxygen-containing ring.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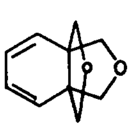
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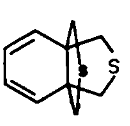
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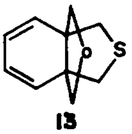
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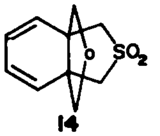
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We have reported the relative directing influence of sulfide, sulfoxide and sulfone rings on Diels–Alder reactions of other dienic and tetraenic propellanes.[4] In due couse we shall have results of X-ray structural investigations of a number of these and additional compounds so that we shall be able to gauge the correctness in prediction of configuration by means of NMR spectroscopy.

EXPERIMENTAL

NMR data measured on a T-60 Varian spectrometer is tabulated.

Diels–Alder reactions The dienic component **4** or **5** was treated with one equivalent of dienophile **3a** or **3b** in CH_2Cl_2. Reaction was instantaneous. When the mono-adduct thus obtained was treated with **3a** or **3b** or when **4** or **5** was treated with 2 equivalents of **3a** or **3b** in CH_2Cl_2, the *bis*-adduct was obtained. The workup involved removal of solvent, trituration with hexane (to remove **4** or **5**) and crystallization.

Compound **8a** m.p. 208–209° (hexane). (Found: M.W. 285. $C_{15}H_{15}N_3O_3$ requires: 285.29). IR ($CHCl_3$): 1765, 1750, 1450, 1400 cm^{-1}. MS M^+, 285 (3); 165 (100); 119 (63).

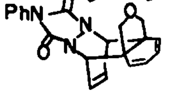
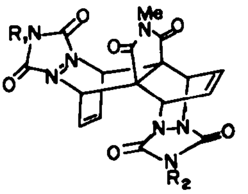
Compound **7a** m.p. 257–258° (benzene). (Found: M.W. 398.1351. $C_{18}H_{18}N_6O_5$ requires: 398.1338). IR ($CHCl_3$): 1770, 1710, 1450, 1400 cm^{-1}. MS M^+, 398 (27); 285 (5); 284 (3); 164 (100).

Compound **7c** m.p. 189–190° (benzene). (Found: M.W. 460.1510. $C_{23}H_{20}N_6O_5$ requires: 460.1495). IR ($CHCl_3$): 1770, 1715, 1400 cm^{-1}. MS M^+, 460 (25); 227 (43); 177 (6); 165 (100); 141 (7); 119 (33).

Compound **7d** was prepared from **8b**^{2} as above, m.p. 182° (sint), 258° (dec). (Found: M.W. 460.1505). IR ($CHCl_3$): 1770, 1720, 1400 cm^{-1}. MS M^+, 460 (50); 227 (100); 177 (5); 165 (81); 141 (9); 119 (70).

Compound **9a** m.p. 246–248° (benzene-hexane). (Found: C, 57.49, H, 4.27, N, 17.22. $C_{16}H_{14}N_4O_4$ requires: C, 58.89; H, 4.32;

NMR data (τ) in $CDCl_3$ (J in Hz)

Compound	Aromatic	Vinylic (all τ)	J(Hz)	Dienic *m*	CHN (all τ)	J(Hz)	CH_2O AB*q*	J(Hz)	NCH_3 (all *s*)	Comments
8a	—	3.50	3.7	4.10	5.30	3.7	6.10,	10	7.10	
							6.45			
8b^2	2.55	3.30	3.0	4.00	5.15	3.0	6.05,	10	—	
							6.45			
7a	—	3.40	3.5	—	5.00	3.5	5.70,		7.00	
		3.70	3.5		5.10	3.5	6.20		7.05	
7b^2	2.54	3.50	3.5	—	5.03		5.70,	9.5	—	
		3.43	3.5				6.25			
7c	2.45	3.40	3.5	—	4.95	3.5	5.65,		7.00	
		3.55	3.5		5.10	3.5	6.22			
7d	2.50	3.30	3.5	—	5.00		5.70,		6.95	
		3.60	3.5				6.20			
	2.37	3.55	3.5	—	4.79	3.5	5.53(s)			in DMSO
	2.57	3.44	3.5	4.27	5.27	3.5	5.51,	11		
							6.47			
9a	—	3.45	3.5	4.10	4.85	3.5	—		6.90	
									7.05	
9b	2.60	3.35	3.5	4.10	4.75	3.5	—		6.90	
6a	—	3.70		—	4.70		—		6.90(3H)	
									7.05(6H)	
6b^2	2.50	3.62	3	—	4.27	3	—		6.95(3H)	in Py
6c	2.55	3.70		—	4.65		—		6.85	
									7.05	
	—	3.45		—	4.80				7.00(6H)	
		3.75							7.04(3H)	
R_1 = Me; R_2 = Ph(**17**)	2.50	3.55			4.70				7.0	
		3.75								
R_1 = Ph; R_2 = Me(**18**)	2.55	3.50			4.70				7.0	
		3.70								

N, 17.17%). IR ($CHCl_3$): 1775, 1720 cm^{-1}. MS 165 (100); 161 (5); 128 (5).

Compound **6a** m.p. 276–277° (dec, CH_2Cl_2), separated from isomer of C_s symmetry by its insolubility in boiling benzene. (Found: C, 52.12; H, 3.94). IR ($CHCl_3$): 1780, 1725 cm^{-1}. MS M$^+$, 439 (11); 164 (100).

Isomer of C_s symmetry (see NMR table for structure): m.p. 252–253° (sint), 240° (dec) (benzene). (Found: C, 51.15; H, 3.90; N, 21.90; M.W. 439.1242). $C_{19}H_{17}N_7O_6$ requires: C, 51.93; H, 3.90; N, 22.31%; M.W. 439.1240). IR ($CHCl_3$): 1780, 1720 cm^{-1}. MS M$^+$, 439 (40); 165 (100); 161 (21).

Compound **6c** m.p. 258–260° (sint), 265° (dec) (benzene). (Found: M.W. 501.1431. $C_{24}H_{19}N_7O_6$ requires: M.W. 501.1397). IR ($CHCl_3$): 1790, 1730, 1400 cm^{-1}. MS M$^+$, 501 (13); 227 (46); 165 (100); 161 (46); 119 (43).

***Reaction of* 10 *with* 3b**. Instantaneous reaction of **10**[5] (47 mg) with **3b** (33 mg) in CH_2Cl_2 (5 ml) gave the adduct as a precipitate (73 mg). It had m.p. > 300° (DMSO). (Found: C, 56.94; H, 2.97; N, 16.90. $C_{20}H_{15}N_5O_3$ requires: C, 57.01; H, 3.59; N, 16.62%). IR (KBr): 1770, 1720 cm^{-1}. NMR ($CDCl_3$ + TFA): τ 2.50 (br, 5 arom H); 3.25 (t, 2 vinylic H); 4.00 (t, $C\underline{H}N$); 6.85 (s, $NC\underline{H}_3$) 6.95 (s, $NC\underline{H}_3$). (Note difference between the two NCH_3 lines). MS 161 (100); 119 (64); 91 (78).

***Reaction of* 11 *with* 3b**. (Carried out by Mr. J. Kalo): Reaction as above with **11** (61 mg) and **3b** (65 mg) in CH_2Cl_2 (5 ml) gave the adduct (120 mg), m.p. 310–311° (dec, chloroform-hexane). (Found: C, 63.47; H, 5.10; N, 12.38; M.W. 339.1242. $C_{18}H_{17}N_3O_4$ requires: C, 63.71; H, 5.05; N, 12.38%; M.W. 339.1219). IR ($CHCl_3$): 1770, 1710, 1400 cm^{-1}. NMR ($CDCl_3$): τ 2.53 (s, 5 arom H); 3.37 (t, 2 vinylic H, J = 3 Hz); 5.07 (t, 2 $C\underline{H}N$, J = 3 Hz); 5.65, 6.28 (ABq, 4 $C\underline{H}_2O$); 6.15, 6.43 (ABq, 4 $C\underline{H}_2O$). (Note difference between the 2 quartets).

Reaction of 12 *with* 3b

(a) A soln of 8, 11-dithia [4.3.3] propell-3-ene[6] (172 mg) in CCl_4 (50 ml) with a trace of dibenzoyl peroxide was irradiated under reflux in an atmosphere of N_2. NBS (155 mg) was added in portions. After 1 hr the whole was cooled to room temp., the solid and solvent removed affording the crude residue (260 mg). DMF (distilled from CaH_2) was added and stirring was maintained for 20 hr at 85°. The soln was poured into water (100 ml) and extracted with ether (5 × 20 ml). The either extract were combined, washed and the solvent removed. A benzene soln of the residue was chromotographed over basic alumina (Grade 1). Elution with hexane gave the diene **12** (68 mg; 44%), m.p. 70–71° (pentane). IR ($CHCl_3$): 2930, 2850, 1430, 1150, 900 cm^{-1}. NMR (CCl_4): τ 3.85–4.45 (m, 4 dienic H); 6.85, 7.15 (ABq, 8 $C\underline{H}_2S$, J = 11 Hz). MS M$^+$, 196 (20); 149 (35); 135 (100); 59 (59).

(b) Instantaneous reaction occurred between **12** (22 mg) and **3b** (20 mg) in CH_2Cl_2 (2 ml). Evaporation gave the product (41 mg; quant), m.p. 239–241° (benzene). (Found: C, 58.44; H, 4.89; N, 10.95; M.W. 371. $C_{18}H_{17}N_3O_2S_2$ requires: C, 58.20; H, 4.61; N, 11.31% M.W. 371.4) IR ($CHCl_3$): 1770, 1700, 1410, 1350 cm^{-1}. NMR ($CDCl_3$): τ 2.57 (s, 5 arom H); 3.40 (t, 2 vinylic H); 5.10 (t, 2 $C\underline{H}N$); 6.40–7.30 (m, 8 $C\underline{H}_2S$). MS M$^+$, 371 (2); 253 (68); 182 (48); 167 (100); 164 (40); 119 (10).

Reaction of 13 *with* 3b

(a) A soln of 8-oxo-11-thia[4.3.3]propell-3-ene mixed with the isomer 2-ene kindly given us by Prof. L. A. Paquette[7] (1.21 g) was brominated as above with NBS (1.2 g + 1.5 g) in CCl_4 (25 ml). After workup as above the crude bromide was dissolved in HMPA (30 ml) and LiCl (0.72 g) and Li_2CO_3 (1.27 g) were added. The whole was maintained at 90° for 16 hr. After workup as above and extraction with pentane repeated chromotography on basic alumina (grade 1), elution with hexane-benzene gave in the first fraction pure diene **13** (29 mg; 2.5%) as an oil NMR ($CDCl_3$): τ 3.80–4.30 (m, 4 dienic H); 6.10 (s, 4 $C\underline{H}_2O$; 6.90–7.20 (m, 4 $C\underline{H}_2S$). MS 182 (10); 181 (28); M$^+$, 180 (20); 149 (44); 135 (83); 119 (66); 104 (88); 60 (100).

(b) Reaction as above with equiv amount of **13** and **3b** gave the adduct **15**, m.p. 261–263°. (CH_2Cl_2–hexane). (Found: C, 60.81; H, 4.49; N, 11.71; S, 9.01; M.W. 355.0935. $C_{18}N_{17}N_3O_3S$ requires: C, 60.80; H, 4.82; N, 11.82; S, 9.02%; M.W. 355.0990) IR (KBr): 1770, 1700, 1410 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (s, 5 arom H); 3.30 (t, 2 vinylic H); 5.10 (t, 2 $C\underline{H}N$); 6.08, 6.18 (ABq, $C\underline{H}_2O$); 6.51, 7.48 (ABq, $C\underline{H}_2S$). MS M$^+$, 355 (39); 227 (100); 197 (11); 178 (11); 151 (28); 135 (13); 119 (48).

(c) Oxidation of **15** with perphthalic acid in the usual way[8] gave **16**, m.p. 330° (CH_2Cl_2-hexane) identical to **16** described below by m. m.p. and spectroscopically.

Reaction of 14 *with* 3b

(a) Oxidation of **13** with perphthalic acid[8] gave the dienic sulfone **14** as an oil in 70% yield. Purification was effected on a preparative alumina plate with hexane as eluent. NMR ($CDCl_3$): τ 3.70–4.50 (m, 4 dienic H); 5.50–6.50 (m, 4 $C\underline{H}_2O$); 6.60–6.90 (m, 4 $C\underline{H}_2SO_2$). MS 212 (24); 153 (46); 135 (74); 119 (47); 118 (100); 117 (100); 115 (90); 105 (100); 104 (100); 92 (100); 79 (96); 77 (99).

(b) Reaction as above with **3b**, after standing overnight gave the adduct **16**, m.p. 330° (CH_2Cl_2–hexane). (Found: M.W. 387.0870. $C_{18}H_{17}N_3O_5S$ requires: 387.0888) IR ($CHCl_3$): 1770, 1720 cm^{-1}. NMR (DMSO-d_6 + TFA): τ 2.50 (s, 5 arom H); 3.30 (t, 2 vinylic H); 4.95 (t, 2 $C\underline{H}N$); 6.05, 6.20 (ABq, 4 $C\underline{H}_2O$), 6.45 (s, 4 $C\underline{H}_2SO_2$). MS M$^+$, 387 (16); 227 (100); 119 (30).

A mixture of **13** and the isomeric 2-ene obtained from Prof. L. A. Paquette[7] was oxidized with perphthalic acid[8] to give a mixture of sulfones but we were unsuccessful in brominating and dehydrobrominating with the view of preparing **14**, using NBS then DMF, Br_2 then NaOMe, Br_2 then Li_2CO_3/HMPA. MS M$^+$, 214 (4); 198 (35); 181 (23); 135 (33); 119 (34); 117 (40); 105 (80); 91 (100).

Compound **17**, R_1 = Me, R_2 = Ph (see NMR table for structure): m.p. 156–158° (benzene-hexane). (Found: C, 56.99; H, 4.09. $C_{24}H_{19}N_7O_6$ requires: C, 57.48; H, 3.88%). IR ($CHCl_3$): 1780, 1720 cm^{-1}. MS 177 (50); 119 (100).

Compound **18** R_1 = Ph, R_2 = Me (see NMR table for structure): m.p. 195–197° (benzene-hexane). (Found: C, 57.23; H, 4.27). IR ($CHCl_3$): 1780, 1720 cm^{-1}. MS 227 (3); 177 (6); 165 (4); 119 (100).

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