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PROPELLANES—LXXIII

CYCLIC OLIGOMERS FROM A [4.3.3]PROPELLENE-*bis*-IMIDE AND 1,ω-DIBROMOALKANES†

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Abstract—Cyclic oligomers were made from the title reactants. These were sometimes accompanied by linear oligomers.

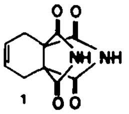
The title *bis*-imide **1** has been prepared from the adduct of 1,3-butadiene and tetracyanoethylene.[1,2] We have bridged the nitrogens in **1** with alkane chains $-(CH_2)_n-$ by stirring the di-K-salt of **1** with $Br(CH_2)_nBr$/DMF at r.t. for 4 days. Since the imide rings are planar *n* must be 7 or higher in order to prepare the mono-bridged compound **2**. However, even with smaller n, as shown in the Table 1, it is possible to prepare cyclic oligomers **3** or in some cases, "trimeric" or "tetrameric" cyclic oligomers in which 3 or 4 propellane molecules are bridged, respectively, by 3 or 4 $-(CH_2)_n-$ chains in addition to **3**. The potentially very interesting first homolog of the "dimeric" series, **3**, n = 1, has not yet been prepared. Treatment of **1** with formaldehyde, not surprisingly, affords a polymer. Open chain oligomers such as **4** and **5** have also been obtained, the highest homolog, e.g. for n = 5 being one containing 5 molecules of **1**, 4 intervening $(CH_2)_n$ bridges and two $-(CH_2)_nBr$ groups at the ends.

Fortunately mass spectrometry was a good analytical tool for the determination of the molecular weight of our products.[3] All products reported herein afforded good combustion results and the expected IR, NMR, and mass spectra.

The products of type **3** could be obtained either from an equimolar mixture of **1** and $Br(CH_2)_nBr$ or from **4** with an additional equivalent of **1**. In the latter case **3** was accompanied by varying amounts of linear oligomers.

EXPERIMENTAL

IR spectra were measured on a Perkin–Elmer model 257 grating spectrophotometer. 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°. The electron energy was maintained at 100 eV. Only the major fragments are listed. All m.ps are uncorrected.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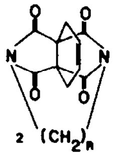
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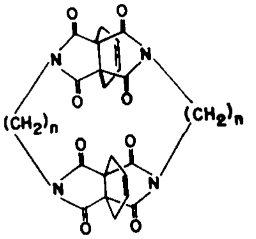
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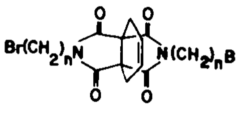
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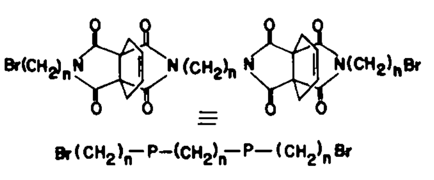
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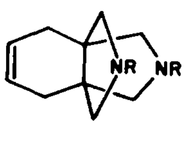
5



6 a R = Me
b = CH_2Ph
c = $OCOCH_2Ph$
d = H

Various model experiments for alkylation of imides

A mixture of 1,2-*cyclohex*-4-*ene*-*imide* (132 mg; 1 eq), n-BuBr (1.23 g; 11 eq), K_2CO_3 (1.57 g; 13 eq) and 18-crown-6 (10 mg) in acetone (25 ml) was stirred at r.t. for 24 hr. After filtration and removal of solvent the residue was treated with hexane. The hexane-soluble material (176 mg, 97%) was the butylimide. Using a ratio of the above imide: bromide: K_2CO_3 of 1:4:5.6 afforded the product under similar conditions in 41% yield. A ratio of 1:1.7:2.3, heating under reflux for 6 hr gave a 73% yield, b.p. 210°/0.6 mm.

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†Part LXXII. P. Ashkenazi, M. Kaftory, T. Sayraç, G. Maier and D. Ginsburg, *Helv. Chim. Acta*, in press.

Table 1.

n	1:1 product		2:2 product		3:3		4:4	
	m.p.(°C)	% yield	m.p.	% yield	m.p.	% yield	m.p.	% yield
2							>275	60
3			115	17^b	158-160	21	181-185	49
4			120-122	46	230-232	5		
5			225	5^b				
6			200-204	60				
7	>275	11^a						
8	248-250	18^a						
9	198-200	19^a						
10	164-166	33^a						
12	140-142	23^a	238-239	4				

a accompanied by linear oligomers

b from *4* and *1*

(Found: N, 6.67; M.W. 207.1274. $C_{12}H_{17}NO_2$ Requires; N, 6.76%; M.W. 207.1250).

The same imide (645 mg; 1 eq); 1.2-dibromoethane (376 mg, 0.47 eq), K_2CO_3 (770 mg; 1.3 eq), 18-crown-6 (20 mg) in acetone (50 ml) stirred at r.t. for 24 hr. Extraction of residue, as above, with hexane gave the 2-bromoethylimide (220 mg). Crystallization of the insoluble residue (benzene-hexane) gave starting imide (325 mg). The mother liquor on a SiO_2 plate with $CHCl_3$ as eluant gave more of the 2-bromoethylimide (356 mg; total yield 38%) and the 1,2-diimidoethane (34 mg; 5%) and more starting imide (57 mg; total recovery 57%).

The 1,2-diimidoethane had m.p. 139–141° after purification as above on a prep. SiO_2 plate. (Found: H, 7.79; M.W. 328.1444. $C_{18}H_{20}N_2O_4$ Requires; N, 8.53%; M.W. 328.1423). IR($CHCl_3$): 1730, 1400, 1150 cm^{-1}. NMR($CDCl_3$): 5.9 (m, 4 vinylic H); 3.8 (s, 4 $C\underline{H}_2N$); 3.1 (m, 4 $C\underline{H}CO$); 2.6–2.3 (m, 8 allylic H).

When the ratio of imide (328 mg), 1,2-dibromoethane (968 mg) and K_2CO_3 (1.87 g) was changed to 1:5:13, with 18-crown-6 (20 mg) in acetone (30 ml), stirring for 24 hr at r.t. and workup as above, the 2-bromoethylimide was obtained by hexane extraction (355 mg; 61%). Chromatography as above gave an oil which crystallized, m.p. 61–63°. Found: N, 5.34; M.W. 257.0095. $C_{10}H_{12}NO_2Br$ Requires: N, 5.42%; M.W. 257.0051). IR($CHCl_3$): 1710, 1400, 1130 cm^{-1}. NMR($CDCl_3$): 5.8 (m, 2 vinylic H); 3.8, 3.5 (A_2B_2, 2 $C\underline{H}_2N$ + 2 $C\underline{H}_2Br$); 3.1 (m, 2 $C\underline{H}CO$); 2.6–2.2 (m, 4 allylic H). MS: *m/e* 259(87); 257(100); 178(17).

Preparation of cyclic oligomers by 1:1 *ratio of reactants*

The *bis*-imide dipotassium salt was prepared by adding K_2CO_3 (165 mg) to the propellane imide (132 mg) in water (5 ml). The solvent was removed in a vacuum (oil pump).

(a) DMF (5 ml), the corresponding dibromide (n = 2; 114 mg) was added to the dry imide salt from 132 mg propellane and stirred 4 days at r.t. After removal of solvent the [4 + 4] product was extracted with EtOAc (109 mg; 74%), m.p. >270° (EtOAc–hexane). (Found: N, 11.30. M.W. 1023 (Rast). $C_{48}H_{40}N_8O_{16}$ Requires: N, 11.38% M.W. 984.9). IR($CHCl_3$): 1770, 1730, 1380, 1360 cm^{-1}. NMR($CDCl_3$): 5.9 (m, 2 vinylic H); 3.8 (m, 4 $C\underline{H}_2N$); 2.7 (m, 4 allylic H).

(b) Dimethylformamide, (10 ml) and the dibromide (n = 3; 121 mg) were added to the dry residue and the whole stirred for 4 days at r.t. After removal of solvent the product was extracted with EtOAc (109 mg; 70%). Extraction with benzene afforded the [3 + 3] cyclic oligomer (32 mg), m.p. 158–160° (benzene–hexane). The benzene-insoluble [4 + 4] cyclic oligomer (68 mg) had m.p. 181–185° (CH_2Cl_2–hexane).

[3 + 3]: (Found: N, 9.97. M.W. 653 (Rast). $C_{39}H_{36}N_6O_2$ Requires: N, 10.77%, M.W. 780.72). IR($CHCl_3$): 1770, 1730, 1360, 1350 cm^{-1}. NMR($CDCl_3$): 5.85 (m, 6 vinylic H); 3.4 (m, 12 $C\underline{H}_2N$); 2.7 (m, 12 allylic H); 2.0 (m, 6 $C\underline{H}_2$). MS: *m/e* 429(100); 341(100); 218(20).

[4 + 4]: (Found: N, 10.16; M.W. 1077 (Rast). $C_{52}H_{48}N_8O_{16}$ Requires: N, 10.77%; M.W. 1040.96). IR($CHCl_3$): 1770, 1730, 1360, 1350 cm^{-1}. NMR($CDCl_3$): 5.9 (m, 8 vinylic H); 3.4 (m, 16 $C\underline{H}_2N$); 2.7 (m, 16 allylic H); 2.0 (m, 16 $C\underline{H}_2$). MS: *m/e* 777(100); 580(25); 301(12.5), 227(10.5).

(c) n = 4 (130 mg). Similar workup gave the [2 + 2] cyclic oligomer (75 mg), m.p. 120–122° (benzene–hexane) and the [3 + 3] product (7 mg), m.p. 210°, 230–232° (dec) (CH_2Cl_2–hexane).

[2 + 2]: (Found: N, 10.03; M.W. 547. $C_{28}H_{28}N_4O_8$ Requires: N, 10.21%; M.W. 548.54). IR($CHCl_3$): 1770, 1730, 1360 cm^{-1}. NMR($CDCl_3$): 6.0 (m, 4 vinylic H); 3.55 (m, 8 $C\underline{H}_2N$); 2.7 (m, 8 allylic H); 1.9–1.4 (m, 8 $C\underline{H}_2$). MS: *m/e* 547(100); 247(20); 219(5).

[3 + 3]: (Found: M.W. 823. $C_{42}H_{42}N_6O_{12}$ Requires: M.W. 822.81) IR($CHCl_3$): 1770, 1730, 1360 cm^{-1}. NMR($CDCl_3$): 5.95 (m, 6 vinylic H); 5.5 (m, 12 $C\underline{H}_2N$); 2.7 (m, 12 allylic H); 2.0–1.4 (m, 12 $C\underline{H}_2$). MS: *m/e* 823(12); 719(18); 637(19); 548(43); 521(100); 492(17); 240(19); 221(27).

(d) n = 6 (146 mg) afforded the [2 + 2] product (108 mg; 59%), m.p. 152–154° (benzene–hexane). When dried in a vacuum it had m.p. 88–90°, resolidifies, 201–204°. (Found: N, 8.74; M.W. 604. $C_{32}H_{38}N_4O_8$ Requires: N, 9.27%; M.W. 604.64). IR($CHCl_3$): 1770, 1730, 1360 cm^{-1}. NMR($CDCl_3$): 5.95 (m, 4 vinylic H); 3.5 (m, 8 $C\underline{H}_2N$); 2.7 (m, 8 allylic H); 2.0–1.1 (m, 16 $C\underline{H}_2$). MS: *m/e* 604(35); 578(15); 560(17); 500(16); 456(16); 383(26); 339(41); 312(43); 303(28); 235(39); 221(100).

(e) n = 7. *Bis*-imide (220 mg); K_2CO_3 (275 mg); dibromide (258 mg), DMF (30 ml), workup as above. EtOAc extraction give product mixture (354 mg), purified on prep. SiO_2 plate eluted twice with CH_2Cl_2. The N,N-*bis*-(7-bromoheptyl)-*bis*-imide was obtained as an oil (25 mg; 4%). (Found: N, 5.71; M.W. 576.0791, 574.0784, 572.0851. $C_{24}H_{34}N_2O_4Br_2$ Requires: N, 4.87%. M.W. 576.0845, 574.0865, 572.0885). IR($CHCl_3$): 1770, 1730, 1350 cm^{-1}. NMR($CDCl_3$): 6.0 (m, 2 vinylic H); 3.5 (q, 8H, $C\underline{H}_2N + C\underline{H}_2Br$); 2.8 (d, 4 allylic H); 2.0–1.3 (m, 20 $C\underline{H}_2$). MS: *m/e* 576(53); 574(100); 572(52); 495(91); 493(84); 399(52); 397(58); 354(91); 352(71); 328(34); 326(35); 235(49); 221(84). A second fraction (35 mg), m.p. >275° was the [1 + 1] product. (Found: N, 8.13, M.W. 316.1417. $C_{17}H_{20}N_2O_4$ Requires: N, 8.86%; M.W. 316.1422). IR($CHCl_3$): 1770, 1730 cm^{-1}. NMR($CDCl_3$): 5.95 (m, 2 vinylic H); 3.6 (t, 4 $C\underline{H}_2N$); 2.8 (d, 4 allylic H); 1.9–1.1 (m, 10 $C\underline{H}_2$). MS: *m/e* 316(100); 287(5); 235(10); 221(7). We did not separate a mixture of higher oligomers (147 mg, 28%).

(f) n = 8 Dibromide (250 mg). Product mixture (314 mg) purified as in d), separated into 2:1 oligomer (29 mg, 48%), 1:1 cyclic product (58 mg; 17.6%) and higher oligomers (96 mg; 17.4%). The 2:1 product, N,N-*bis*-(8-bromooctyl)-*bis*-diimide was an oil. (Found: N, 3.79; M.W. 604.1166, 602.1180, 600.1179. $C_{26}H_{38}N_4O_4Br_2$ Requires: N, 4.65%; M.W. 604.1159, 602.1178, 600.1197). IR($CHCl_3$): 1770, 1730, 1350 cm^{-1}. NMR($CDCl_3$): 6.0 (t, 2 vinylic H); 3.5 (q, 8 $C\underline{H}_2N + C\underline{H}_2Br$); 2.8 (d, 4 allylic H), 2.0–1.3 (m, 24 $C\underline{H}_2$). MS: *m/e* 604(72); 602(98); 600(58); 479(27); 477(72); 414(24); 413(82); 412(27); 411(769); 367(46); 342(46) 340(39); 235(55); 221(100).

[1 + 1] cyclic product, m.p. 248–250° (CH_2Cl_2-hexane). (Found, N, 7.69; M.W. 330.1554. $C_{18}H_{22}N_2O_4$ Requires: N, 8.48%; M.W. 330.1579). IR($CHCl_3$): 1770, 1730 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 2 vinylic H); 3.6 (t, 4 $C\underline{H}_2N$); 2.8 (d, 4 allylic H); 1.9–1.0 (m, 12 $C\underline{H}_2$). MS: *m/e* 330(100); 235 (38); 221(17). Analysis of the higher oligomer mixture for Br shows the presence of a 2:3 and 3:4 linear oligomer (i.e. 2 and 3 propellane moieties, respectively).

(g) n = 9, (286 mg) afforded as above crude mixture (317 mg). Separation as above gave 2:1 product (34 mg; 5.3%), [1 + 1] product (64 mg; 18.6%), and higher oligomers (54 mg; 9.4%).

2:1 product was as oil. (Found: C, 53.64; H, 6.79; M.W. 632.1409, 630.1441, 628.1541. $C_{28}H_{42}N_2O_4Br_2$ Requires: C, 53.33; H, 6.7%; M.W. 632.1470, 630:1491, 628.1511). IR($CHCl_3$): 1770, 1730, 1360 cm^{-1}. NMR($CDCl_3$): 6.0 (t, 2 vinylic H); 3.5 (q, 8 $C\underline{H}_2N + C\underline{H}_2Br$); 2.75 (d, 4 allylic H); 1.9–1.1 (m, 28 $C\underline{H}_2$). MS: *m/e* 632(70); 630(97); 628(63); 551(80); 549(63); 427(37); 425(43); 382(100); 380(43); 221(37).

[1 + 1] cyclic product had m.p. 197–198° (CH_2Cl_2–hexane) (Found: N, 7.88; M.W. 344.1745 (MS), also determined by X-ray method. $C_{19}H_{24}N_2O_4$ Requires: N, 8.13%; M.W. 344.1736). IR($CHCl_3$): 1770, 1730, 1360 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 2 vinylic H); 3.65 (t, 4 $C\underline{H}_2N$); 2.8 (d, 4 allylic H); 2.0–1.1 (m, 14 $C\underline{H}_2$). MS: *m/e* 344(100); 235(14); 221(15).

(h) n = 10. (302 mg) gave crude mixture (378 mg) separated into 2:1 oligomer (16 mg; 2.4%), [1 + 1] cyclic product (117 mg; 32.7%); higher oligomers (63 mg; 11%).

2:1 product was an oil. (Found: C, 54.98; H, 7.40; M.W. 660.1848, 658.1820, 656.1800. $C_{30}H_{46}N_2O_4Br_2$ Requires: C, 54.71; H, 7.64%; M.W. 660.1784, 658.1804, 656.1824). IR($CHCl_3$): 1770, 1730, 1355 cm^{-1}. NMR($CDCl_3$): 6.0 (t, 2 vinylic H); 3.45 (q, 8 $C\underline{H}_2N + C\underline{H}_2Br$); 2.7 (t, 4 allylic H); 2.0–1.2 (m, 32 $C\underline{H}_2$). MS: *m/e* 660(48); 658(74); 656(34); 616(40); 614(77); 612(92); 579(56); 577(50); 441(69); 439(44); 221(100).

[1 + 1] product had m.p. 164–166° (CH_2Cl_2–hexane). (Found: N, 7.26; M.W. 358.1870. $C_{20}H_{26}N_2O_4$ Requires: N, 7.82%; M.W. 358.1892). IR($CHCl_3$): 1770, 1730, 1355 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 2 vinylic H); 5.55 (t, 4 $C\underline{H}_2N$); 2.75 (t, 4 allylic H); 1.9–1.1 (m, 16 $C\underline{H}_2$). MS: *m/e* 358(100); 332(16); 324(17); 314(11); 289(12); 261(13); 248(16); 234(51); 221(82).

(*i*) *n* = 12. (327 mg) gave mixture (353 mg) separated with $CHCl_3$ as eluent into 2:1 oligomer (46 mg; 6.4%), [1 + 1] cyclic product (89 mg; 23%), [2 + 2] cyclic oligomer (13.6 mg; 3.5%) and higher oligomers (122 mg; 18.7%).

The 2:1 product had m.p. 81–82° (chloroform–hexane). Its analysis and spectral data appear below.

[1 + 1] cyclic product had m.p. 140–142° (benzene–hexane). (Found: N, 6.85; M.W. 386.2171. $C_{22}H_{30}N_2O_4$ Requires: N, 7.25%; M.W. 386.2204, determined also by X-ray method.) IR($CHCl_3$): 1770, 1730, 1350 cm^{-1}. NMR($CDCl_3$): 5.9 (t, 2 vinylic H); 3.55 (t, 4 $C\underline{H}_2N$); 2.75 (d, 4 allylic H); 1.9–1.1 (m, 20 $C\underline{H}_2$). MS: *m/e* 386(100); 235(7); 221(17).

[2 + 2] cyclic oligomer had m.p. 238–239° (CH_2Cl_2–hexane), see below.

General procedure for preparing 1:2-*adducts*

The [4.3.3] *bis*-imide was treated with an equiv. amount of K_2CO_3 for formation of the di-K-Salt in water. Removal of the water in a vacuum, trituration of the salt with ether and drying at oil pump vacuum gave the dry salt. This was treated with 8 eq of the corresponding dibromide and dry DMF. The whole was stirred magnetically for 5 days at r.t. The salt gradually dissolves with only a light suspension of solid remaining. DMF was removed at the water pump (45–60°) and the residue was extracted with EtOAc. Washing with 10% HCl, drying the organic phase with $MgSO_4$ and removal of solvent afforded the product mixture. This was separated on a column of silica (Woelm, active, 70–150 mesh) using CCl_4. Excess dibromide is eluted first. With $CHCl_3$ the next product is the 1:2 compound (55–75%) followed by the 2:3 product (5–15%). In small batches prep. silica plates (Merck; 20 × 20 cm, silica gel (60F-254) are used, using $CHCl_3$ as eluent.

(a) n = 2. *Bis*-imide (44 mg), K_2CO_3 (55 mg), DMF (3 ml), dibromide (300 mg) afforded after $CHCl_3$ extraction a mixture (109 mg). Separation of components on prep SiO_2 plate with $CHCl_3$ as eluent gave the N,N-*bis*-(2-bromoethyl)-*bis*-imide, the [2 + 2] cyclic oligomer and the 2:3-linear oligomer.

The 1:2 product had m.p. 137–139° (Found: N, 6.25; M.W. 435.9278, 433.9310, 431.9331. $C_{14}H_{14}N_2O_4Br_2$ Requires: N, 6.45%; M.W. 435.9280, 433.9300, 431.9321). IR($CHCl_3$): 1780, 1750, 1380, 1360, 1110 cm^{-1}. NMR($CHCl_3$): 5.95 (t, 2 vinylic H); 3.9, 3.6 (A_2B_2, 4 $C\underline{H}_2N$ + 4 $C\underline{H}_2Br$); 2.8 (d, 4 allylic H). MS: *m/e* 435(45); 433(100); 431(50).

The 2:3 product was an oil (Found: M.W. 681.9955, 679.9985, 677.9061. $C_{26}H_{24}N_4O_8Br_2$ requires 681.9920, 679.9940, 677.9938). IR($CHCl_3$): 1770, 1740, 1350 cm^{-1}. NMR($CDCl_3$): 5.9 (m, 4 vinylic H); 3.9, 3.6 (A_2B_2, 4 $C\underline{H}_2N$ + 4 $C\underline{H}_2Br$); 3.7 (s, 4 $C\underline{H}_2N$); 2.7 (m, 8 allylic H). MS: *m/e* 681(47); 679(100); 677(44); 599(10).

(b) n = 3. 1:2 adduct was an oil (53% yield). (Found: M.W. 461.9613. $C_{16}H_{18}N_2O_4Br_2$ requires M.W. 461.9613). IR($CHCl_3$): 1775, 1740, 1350 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 2 vinylic H); 3.7 (t, 4 $C\underline{H}_2Br$); 3.3 (t, 4 $C\underline{H}_2N$); 2.8 (d, 4 allylic H); 2.15 (quintet, 4 $C\underline{H}_2$). MS: *m/e* 462(100); 190(13); 188(11); 162(16); 105(28).

2:3 adduct, oil (6%). (Found: M.W. 724.0362, 722.0462, 720.0445. $C_{29}H_{30}N_4O_8Br_2$ Requires M.W. 724.0390, 722.0411, 720.0430). IR($CHCl_3$): 1780, 1740, 1350 cm^{-1}. NMR($CDCl_3$): 6.0 (t, 4 vinylic H);, 3.75 (t, 4 $C\underline{H}_2Br$); 3.4 (t, 8 $C\underline{H}_2N$); 2.8 (d, 8 allylic); 2.4–1.85 (m, 6 $C\underline{H}_2$). MS: *m/e* 722(100); 720(44); 644(14); 643(28); 190(11); 188(13); 162(14); 105(30).

(c) n = 5. 1:2 adduct was oil (70%). (Found: N, 5.60; Br, 30.14; M.W. 520.0174, 518.0169. $C_{20}H_{26}N_2O_4Br_2$ Requires: N, 5.40; Br, 30.88%; M.W. 520.0219, 518.0237). IR($CHCl_3$): 2960, 2870, 1810, 1770, 1740 cm^{-1}. NMR($CDCl_3$): 6.0 (t, 2 vinylic H); 3.7–3.3 (m, 8 $C\underline{H}_2Br + C\underline{H}_2N$); 2.8 (d, 4 allylic H); 2.15–1.5 (m, 12 $C\underline{H}_2$). MS: *m/e* 518(100); 439(13); 300(18); 221(11); 188(2); 162(37); 105(62).

2:3 Adduct had m.p. 105° (13%). (Found: M.W. 806.1257, 804.1039. $C_{35}H_{42}N_4O_8Br_2$ requires M.W. 806.1359, 804.1016). IR($CHCl_3$): 1770, 1740 cm^{-1}.

NMR($CDCl_3$): 6.0 (t, 4 vinylic H); 3.7–3.2 (m, 12 H, $C\underline{H}_2Br^+$ $C\underline{H}_2N$); 2.8 (d, 8 allylic H); 2.1–1.3 (m, 18 $C\underline{H}_2$). MS: *m/e* 806(27); 518(36); 300(27); 162(100).

[2 + 2] cyclic oligomer had m.p. 225°. (Found: M.W. 576.2028. $C_{30}H_{32}N_4O_8$ requires M.W. 576.2221). IR(KBr): 2940, 2860, 1720 cm^{-1}. NMR($CDCl_3$): 6.05 (t, 4 vinylic H); 3.8–3.4 (m, 8 $C\underline{H}_2Br + C\underline{H}_2N$); 2.8 (d, 8 allylic H); 1.9–1.2 (m, 12 $C\underline{H}_2$). MS: *m/e* 576(58); 508(12); 207(19); 188(79); 160(16); 144(100).

(d) n = 6. 1:2 adduct, m.p. 46–47°. (Found: N, 5.15; Br, 29.13; M.W. 548.0525, 546.0492, 544.0477. $C_{22}H_{30}N_2O_4Br_2$ Requires: N, 5.13; Br, 29.30%; M.W. 548.0532, 546.0551, 544.0572). IR(KBr): 2940, 2860, 1760, 1725 cm^{-1}. NMR($CDCl_3$): 6.0 (t, 2 vinylic H); 3.7–3.3 (m, 8 $C\underline{H}_2Br + C\underline{H}_2N$); 2.8 (d, 4 allylic H); 2.0–1.3 (m, 16 $C\underline{H}_2$). MS: *m/e* 546(96); 465(17); 385(24); 383(28); 312(22); 235(11); 221(19); 160(20); 105(100).

(e) n = 12. 1:2 adduct, m.p. 71° (75%). (Found: N, 3.95; Br, 22.11; M.W. 716.2373, 714.2413, 712.2408. $C_{34}H_{54}N_2O_4Br_2$ Requires: N, 3.92; Br, 22.41%; M.W. 716.2409, 714.2430, 712.2412). IR($CHCl_3$): 2930, 2860, 1770, 1730 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 2 vinylic H); 3.7 (t, 4 $C\underline{H}_2Br$); 3.4 (t, 4 $C\underline{H}_2N$); 2.75 (d, 4 allylic H); 1.3 (m, 40 $C\underline{H}_2$). MS: *m/e* 714(83); 633(100); 467(42); 221(50); 162(42); 105(50).

General procedure for preparing [2 + 2] *cyclic oligomers*

The dipotassium salt was prepared as above. A soln of the 1:2 adduct in DMF was added and the whole was magnetically stirred at r.t for 4 days. After workup as above the solid residue was separated as above by prep TLC, or by crystallization.

The [4 + 4] cyclic oligomer appeared in a 14 day reaction mixture, m.p. >270° (EtOAc–hexane). (Found: N, 10.03, M.W. 1023 (Rast). $C_{48}H_{40}N_8O_6$ requires N, 11.38; M.W. 984.88). IR($CHCl_3$): 1770, 1730, 1380, 1360 cm^{-1}. NMR($CDCl_3$): 5.9 (m, 8 vinylic H); 3.8 (m, 16 $C\underline{H}_2N$); 2.7 (m, 16 allylic H).

No useful products were obtained when attempted insertion of a one carbon bridge was carried out on the *bis*-imide using CH_2Br_2, CH_2I_2, CH_2O, phosgene. Formaldehyde gave, not surprisingly a polymer, in principle reminiscent of Bakelite.

[2 + 2] cyclic oligomer, n = 12, m.p. 236° (Found: N, 6.23; M.W./2 386.2210. $C_{22}H_{30}N_2O_4$ Requires: N, 7.25%; M.W./2 386.2205). IR(KBr): 2930, 2850, 1760, 1730 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 4 vinylic H); 3.8–3.45 (m, 8 $C\underline{H}_2N$); 2.8 (d, 8 allylic H); 1.3 (m, 40 $C\underline{H}_2N$). MS (low resolution): *m/e* 772(100); 221(20); 162(27); 160(16); 105(32).

8,11-*Dibenzyl*-8,11-*diaza*-7,9,10,12-*tetraoxa*[4.3.3]*propell*-3-*ene*

The di-K salt of the *bis*-imide on (220 mg) was prepared as above with K_2CO_3 (140 mg). It was heated under reflux for 3 hr with benzyl chloride (20 ml) with magnetic stirring. The huge excess of benzyl chloride was removed in a vacuum and the solid residue was taken up in CH_2Cl_2, washed with water (2x), dried (Na_2SO_4), filtered and the solvent removed. The *bis*-benzyl derivative (380 mg; 95%) had m.p. 192–193° (glacial AcOH). (Found: C, 72.00; H, 5.00; N, 7.00; M.W. 400.1388. $C_{24}H_{20}N_2O_4$ Requires: C, 71.66; H, 5.02; N, 6.95%; M.W. 400.1388). IR(KBr): 3030, 1760, 1725 cm^{-1}. NMR($CDCl_3$): 7.25 (s, 10 arom H); 5.95 (t, 2 vinylic H); 4.7 (s, 4 $PhC\underline{H}_2$); 2.75 (d, 4 allylic H); MS: *m/e*: 400(100); 310(4); 309(10); 181(41); 162(11).

Reduction

A mixture of the dibenzylimide (0.8 g), LAH (1 g) and dry freshly distilled THF (50 ml) was heated under reflux for 36 hr with magnetic stirring. After alkaline decomposition (5% NaOH) the usual workup gave crude 8,11-dibenzyl-8,11-diaza[4.3.3]propell-3-ene, **6c** (630 mg). Percolation of a hexane solution through a column (15 g) of active alumina (Woelm, 70–150 mesh) gave the pure product, oil (580 mg; 84%). (Found: M.W. 344.2250. $C_{24}H_{28}N_2$ Requires M.W. 344.2251). IR($CHCl_3$): 2900, 2800 cm^{-1}. NMR($CDCl_3$): 7.3 (s, 10 arom H); 5.8 (t, 2 vinylic H); 3.5 (s, 4 $PhC\underline{H}_2$); 2.54–2.34 (quartet, 8 $C\underline{H}_2N$); 2.10 (d, 4 allylic H). MS: *m/e* 344(31); 253(100); 225(20); 210(28); 145(16); 119(46); 105(99.9).

Hydrogenolysis of the N–Bz bond could not be effected with Pd/H_2 with Pd/C/H_2 at 3 atm pressure or with Na/NH_3. Using Pd/C the cyclohexene double bond was reduced.

Corresponding bis-*carbobenzoxy derivative*

The cesium salt of 1 (220 mg) was prepared with cesium carbonate (400 mg) in water (5 ml).[4] After removal of water and drying in a high vacuum the salt was suspended in a soln of benzyl chloroformate (0.6 ml) in dry THF (15 ml) with cooling at 0°. The salt dissolved and a very fine suspension was formed. After stirring at 0° for 3 hr, EtOAc (50 ml) was added and the mixture was extracted with a sodium potassium acid phosphate buffer at pH 6.5. The organic phase was dried (Na_2SO_4). Removal of solvent gave **6c** (395 mg; 80%), needles, m.p. 148° (MeOH). (Found: C. 63.38; H, 3.92; N, 6.00; M.W. 488.1011. $C_{26}H_{20}N_2O_8$ Requires: C, 63.76; H, 4.09; N, 5.73%; M.W. 488.1218). IR(KBr): 3040, 1840, 1790, 1730, 1250 cm^{-1}. NMR($CDCl_3$): 7.35 (s, 10 arom H); 5.9 (t, 2 vinylic H); 5.3 (s, 4 $PhC\underline{H}_2$); 3.8 (d, 4 allylic H); MS: *m/e* 488(3.3); 353(17); 247(72); 180(100); 107(83); 105(55.5).

Reduction[5]

A mixture of the dicarbobenzoxy-*bis*-imide (500 mg), LAH (400 mg) in dry THF (50 ml) was stirred under N_2 and reflux for 4 days. After workup as above the product, **6a** was obtained as an oil (105 mg; 50%). It gave a yellow picrate, m.p. 195°, and was identified by comparison with an authentic sample[6] (Found: M.W. 192.1609. $C_{12}H_{20}N_2$ Requires: M.W. 192.1626). NMR($CDCl_3$): 5.8 (t, 2 vinylic H); 2.6–2.4 (quar, 8 $C\underline{H}_2N$); 2.2 (s, 6 $NC\underline{H}_3$); 2.1 (d, 4 allylic H). MS: *m/e* 192(12); 178(11); 160(30); 146(25); 134(100).

8,11-*Diaza*[4.3.3]*propell*-3-*ene*

The *bis*-imide 1 (1 g), LAH (1 g) in dry THF (60 ml) were heated under reflux with stirring for 6 days. After the usual workup the diamine **6d** was obtained as an oil (420mg; 50%), b.p. 65° (0.05 torr). (Found: M.W. 164.1313. $C_{10}H_{16}N_2$ Requires: M.W. 164.1312). IR(neat): 3350 (br), 2920, 2860 cm^{-1}. NMR($CDCl_3 + D_2O$): 5.8 (t, 2 vinylic H; 4.82 (s, 2 $N\underline{H}$); 2.85 (s, 8 $C\underline{H}_2N$); 2.1 (d, 2 allylic H). MS: *m/e* 164(8); 147(77); 146(100); 134(78); 133(20);122(29); 120(100); 105(53). The product is unstable in air, turns red, then black. Its oxalate was prepared in EtOH. The colorless salt formed transparent plates, m.p. 230° (dec, water). (Found: N, 9.20. $C_{12}H_{18}N_2O_4.3H_2O$ Requires: N, 9.09%. $C_{12}H_{18}N_2O_4.2H_2O$ Requires N, 9.65%). Its X-ray structure was determined[7] and showed the presence of $2H_2O$ per molecule of oxalate salt.

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