Tetrahedron Vol 37, pp 151 to 160
Pergamon Press Ltd., 1981. Printed in Great Britain

0040-4020/81/0101-0151/$02.00/0

PROPELLANES-LV

SYNTHESIS AND DIELS-ALDER REACTIONS OF TETRAENIC PROPELLANE IMIDES DERIVED FROM ESTERS OF α-AMINOACIDS[a]

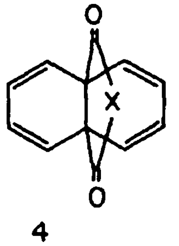
M. PELED and D. GINSBURG*

Department of Chemistry—Israel Institute of Technology, Haifa, Israel

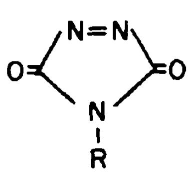
(*Received in UK 5 November 1979*)

Abstract—Tetraenic propellane imides were prepared from a variety of α-aminoesters. The extent to which these were attacked by 4-substituted-1,2,4-triazolinediones from the side *syn* or *anti* to the imide ring was in most cases determined by the size of the substituent in the imide ring although some exceptions occur.

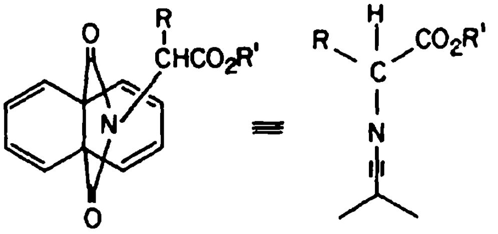
Practically all of the propellane molecules we have described are *meso*-compounds. If one wishes to prepare chiral propellanes, e.g. in a system such as **1** (which is *meso*) all one needs to do is to place a substituent, e.g. at one or the other of the carbons marked with an arrow (or for that matter, at both). But, of course, a separate synthesis would be required to prepare each substituted propellane. An easier way to introduce chirality into a propellane molecule could be brought about by reacting a *meso*-molecule with a chiral one under conditions which avoidn racemization of the latter, e.g. by reaction of the versatile and readily available intermediate **2** with an ester of an α-aminoacid **3**, also readily available. Thus chirality is introduced by a chiral center attached not directly to the propellane skeleton but to a side-chain thereon. We had certain designs upon the chiral compounds but we also had a more immediate application within the framework of super-position of steric effects upon the electromic ones responsible for secondary orbital interactions studied in another connection.[1]



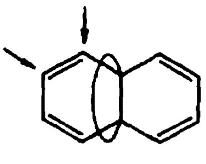
4



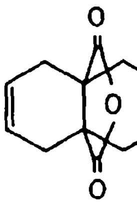
5



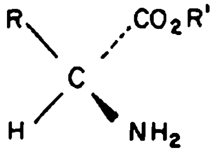
6



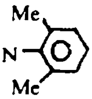
1



2



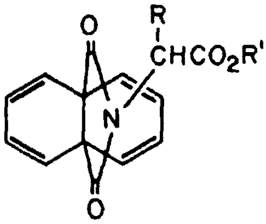
3

We have attempted to be convincing in our interpretation that exclusive *syn*-attack of compounds of type **4** by dienophiles of type **5** is due to secondary orbital interactions between the CO-π^* (LUMO) of the dienic component **4** with the antisymmetric n_--combination of lone pair orbitals (HOMO) in the dienophile **5**.[2] Superimposing a steric factor by suitable variation in the structure of X in **4**, upon this electronic one, ought to reduce the efficiency of the latter and afford significant amounts of *anti*-attack in addition to *syn*-attack. This has indeed been found in X=N—CH$_2$C(CH$_3$)$_3$,  and in the lactone analog of the anhydride **4**, X=O.[4] In our present compounds, resulting from the dienic **2** and **3** followed by conversion into the tetraenic **6**, we may vary the size of R and R' and thus perhaps construct more and less effective umbrellas covering more and less effectively the *syn*-faces of the cyclohexadiene rings towards attack by dienophiles.

---

[a] Part LIV. P. Ashkenazi, M. Kaftory, W. Grimme, K. eger, E. Vogel and D. Ginsburg, *Bull. Soc. Chim. Belges* in ess.

Table 1



	Mono-adduct syn/anti r.t.	Bis-adduct C_{2v}/C_s r.t.	Mono-adduct syn/anti −78 C	Bis-adduct C_{2v}/C_s −78 C
R=H; R′=CH_3	∞	—	—	—
R=H; R′=n−C_6H_{13}	∞	—	—	—
R=CH_3; R′=CH_3		2.5	∞	–
R=CH_3; R′=exo-Bornyl		3.2	—	5
R=CH_3; R′=*t*-Bu		—	0.8	0.7
R=$CH_2CH(CH_3)_2$; R′=CH_3	1.2	—	2.2	—
R′=n-C_6H_{13}	1.0	—	1.9	—
R′=exo-Bornyl	1.2	—	—	1.9
R′=*t*-Bu	—	0.8	—	1.7

We anticipated that the larger R and R′, the more would *anti*-attack replace the exclusive *syn*-attack obtained when the X group in **4** does not exert any significant steric repulsion towards dienophole approaching from the *syn*-direction. However, although this is more or less correct with respect to R (this point will be qualified in the subsequent paper). the size of R′ does not appear to matter all that much.

We see in Table 1 that the reaction temperature makes some difference. The ratio of *syn*:*anti* mono-adducts (**8**:**11**) is given at room temperature and at −78°C. The ratio of C_{2v}:C_s *bis*-adducts (**9**:**12**) is also given.

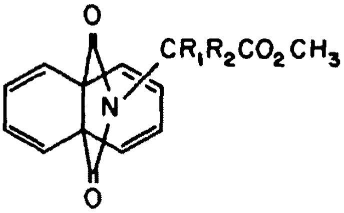
When R=H the ester substituent R′ has no influence; only the *syn*-adduct is obtained exactly analogous to the result for **4**, X=NMe.[5] When R=Me the ester substituent has a greater steric effect and the larger R′ it appears as a crude generalization that more *anti*-attack is obtained. But when R=$CH_2CH(CH_3)_2$, the ester substituent hardly makes a difference and the ratio of syn:anti-attack is almost the same. We assume free rotation about the N−CHR_1CO_2R' bond withir the time scale of reaction with dienophile.

Table 2 compares the effect of size of R_1 and R_2 within a series of methyl esters.

Table 2 indicates that the effect of $CH_2CO_2CH_3$ is not much different from CH_3 but that of $CH_2CH(CH_3)_2$ is somewhat greater than CH_3 and more *anti*-attack results. One would anticipate that i both R_1 and R_2 are not H, one should obtain more *anti*-attack. Thus **14** in which R_1=R_2=CH_3 behaves quite unexpectedly, not only in that exclusive *syn*-attack is found but also in further reaction of **15** to afford *bis*-adducts. Usually the second mole o dienophile adds exclusively *syn* but in this particula case **15** was attacked both *syn* and *anti* to afford **17** and **16**, respectively.

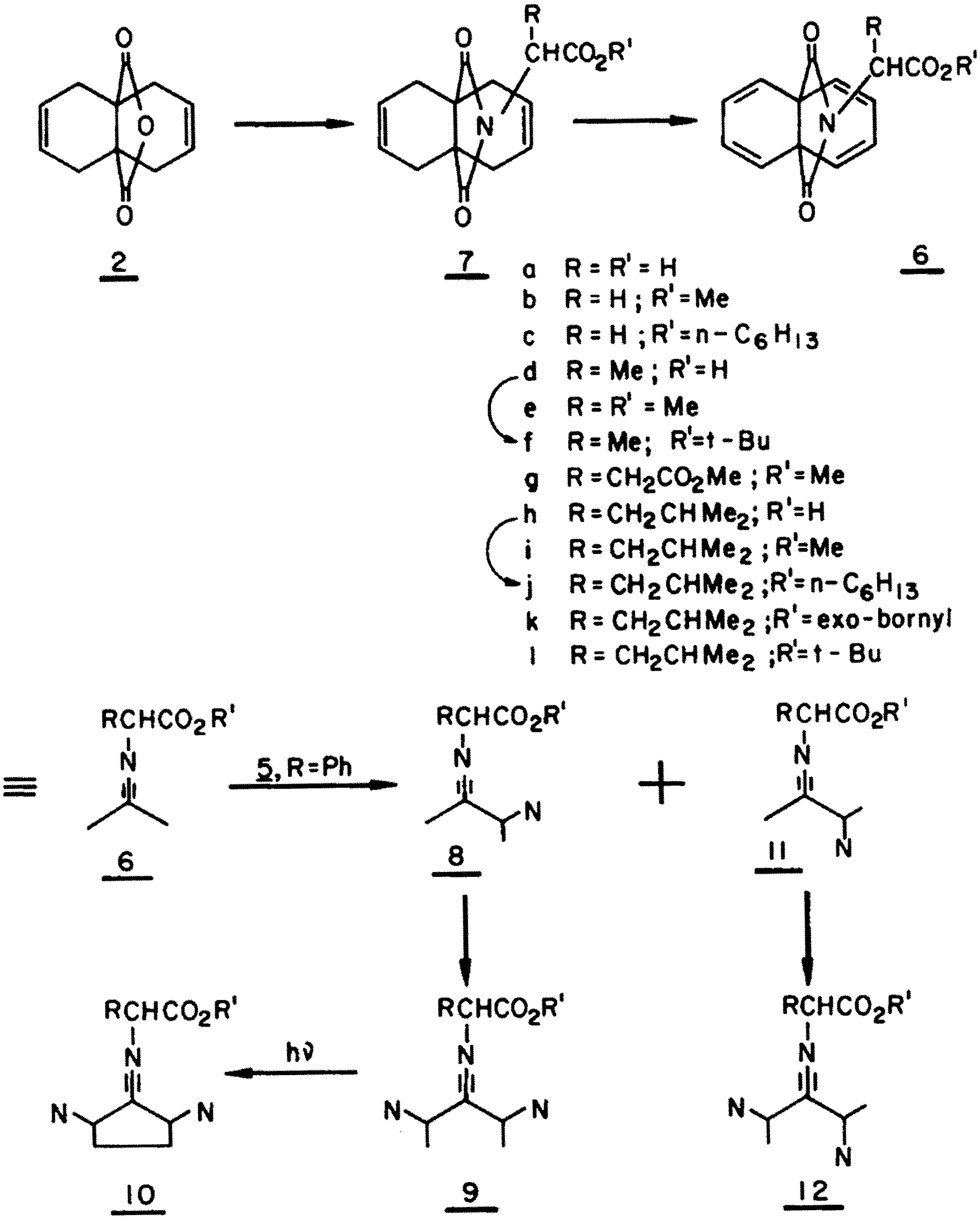
We prepared **19** from **13d**. R_1=R_2=−$(CH_2)_4$-t compare its behavior to that of **14**. Attack in this cas was not exclusively *syn* en route to mono-adduct bu the second mole of dienophile did attack only from th *syn*-direction. Thus **19** does not behave as surprisingl

Table 2

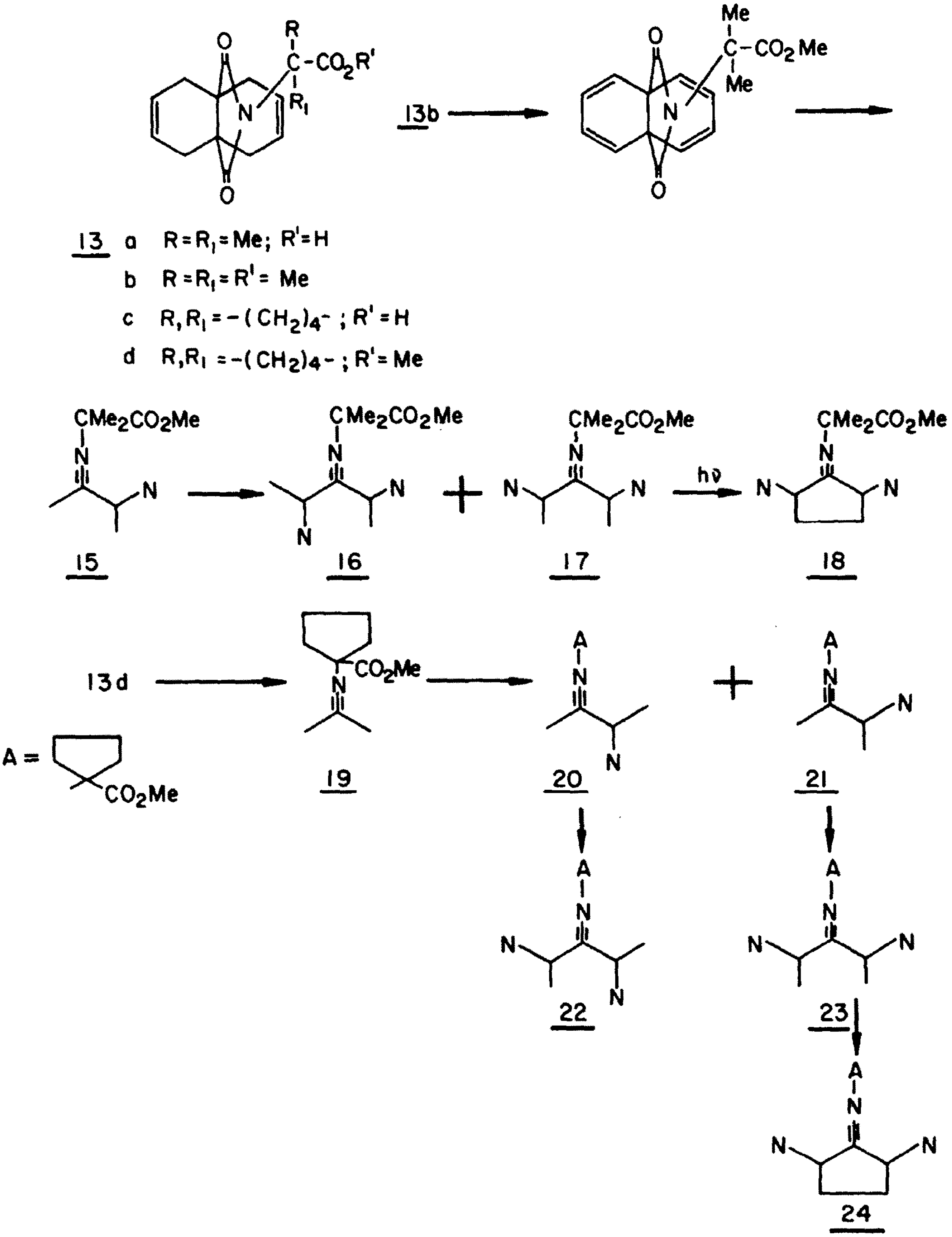


	Mono-adduct syn/anti r.t.	Mono-adduct syn/anti −78°
R_1=R_2=H	∞	—
R_1=H; R_2=CH_3	2.5	∞
R_1=H; R_2=$CH_2CO_2CH_3$	2.7	4.7†
R_1=H; R_2=$CH_2CH(CH_3)_2$	1.2	2.2
R_1=R_2=CH_3	∞	—
R_1=R_2=−$(CH_2)_4$−	3.5	—

†The mono-adducts could not be separated. The ratio is based on the NMR signals for the CH_3O_2C groups.


2
7
6
a $R = R' = H$
b $R = H$; $R' = Me$
c $R = H$; $R' = n-C_6H_{13}$
d $R = Me$; $R' = H$
e $R = R' = Me$
f $R = Me$; $R' = t-Bu$
g $R = CH_2CO_2Me$; $R' = Me$
h $R = CH_2CHMe_2$; $R' = H$
i $R = CH_2CHMe_2$; $R' = Me$
j $R = CH_2CHMe_2$; $R' = n-C_6H_{13}$
k $R = CH_2CHMe_2$; $R' = exo-bornyl$
l $R = CH_2CHMe_2$; $R' = t-Bu$
≡
5, R=Ph
hν
6
8
11
9
10
12

Scheme 1


R
C-CO2R'
R1
O
N
O
13b
Me
C-CO2Me
Me
13 a R=R1=Me; R'=H
b R=R1=R'= Me
c R,R1=-(CH2)4-; R'=H
d R,R1=-(CH2)4-; R'=Me
CMe2CO2Me
N
15
16
17
hν
18
13d
CO2Me
19
A
20
21
A = CO2Me
22
23
24

Scheme 2

as **14**, whose reason for such behavior is as yet not clear to us.

Scheme 1 summarizes the synthetic sequence starting from **2** and a number of α-amino-acids and their esters.

Scheme 2 summarizes analogous reaction sequences for α,α-disubstituted amino-acids and esters.

EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer 237 spectrometer, in chloroform unless otherwise stated. NMR spectra were measured on a Varian T-60 or Bruker WP-60 instrument, in $CDCl_3$ unless otherwise stated, TMS as standard, signals given in τ values. Mass spectra were measured on a Varian MAT-711 spectrometer. M.ps are uncorrected. Organic solns were dried over $MgSO_4$ and solvents were removed in a flash evaporator at the water pump.

4-Phenyl-1,2,4-triazoline-3,5 dione is abbreviated PTD.

Chromatographic separations on 20 × 20 cm prep plates were prepared from 70 g silica gel, 60 PF 254 using about 150 mg of material per plate. The eluents were mixtures of EtOAc–hexane in different proportions.

The amino-acids or esters were commercial samples unless otherwise stated. They were all of the L-series.

Preparation of anhydride **2**

Into a liter pressure tube were introduced acetylene-dicarboxylic acid (100 g), hydroquinone (10 g) and dioxan (80 ml). Butadiene (*ca* 200 ml) was liquified into the tube with liquid N_2 cooling. The whole was heated in a rocking autoclave (Aminco) at 190° for 10 hr. After cooling the whole was transferred into a 3-necked flask and volatile material removed at 60° in a flash evaporator overnight. 10% KOHaq (1 liter) was added and the whole was heated under reflux for 1 hr. After cooling to 50–60°, activated carbon (50 g) was added with mechanical stirring for 30 min. The solid was removed by filtration and the filtrate was carefully acidified with 10% HCl. The diacid precipitated and was removed by filtration. It was added to 1 liter water and solid Na_2CO_3 was added carefully with mech stirring until complete dissolution. Carbon black (50 g) was again added, stirring maintained another 30 min and the whole filtered. The filtrate was again acidified and the product collected by filtration. If the product still contains (oily sticky) polymer the Na_2CO_3 step is repeated.

The diacid and benzene (500 ml) were placed in a 3-necked flask and the water was removed azeotropically with mech stirring. After cooling and filtration the product is dried in a vacuum, yield 45–50% based on acetylene-dicarboxylic acid.

Cyclization to the anhydride **2** is affected by heating under reflux in Ac_2O (5 ml per g of diacid). Traces of Ac_2O are removed at the oil pump (0.1 mm) and the solid residue is distilled at 110°/0.01 mm. The distillate is dissolved in benzene and filtered through a column of neutral alumina in order to remove traces of polymer, yield of colorless and odorless **2** from diacid, 85–90%.

General procedure for preparing dienic substituted propellane imides, **7a**

(a) Into a flask equipped with a Dean–Stark condenser were placed benzene or toluene (200 ml), triethylamine or pyridine (5 ml), the anhydride **2** (3.5 mmol) and the α-amino-acid (3.8 mmol) and the whole was heated under reflux overnight. After cooling and filtration the product was extracted with 10% Na_2CO_3 aq (3 × 50 ml). The cold soln was carefully acidified with HCl. The product was extracted into chloroform and after drying the solvent was removed. The product **7a** was recrystallized from a suitable solvent.

(b) The anhydride **2** (0.5 mmol) and the α-amino-acid (0.4 mmol) were powdered together with mortar and pestle, transferred to a test tube and heated with several drops of pyridine until a homogeneous amber-colored melt was obtained. After cooling the melt was dissolved in chloroform and filtered. The product was extracted from the chloroform soln with 10% Na_2CO_3 aq (3 × 50 ml). The cold aq extract was acidified carefully with 10% HCl and the product extracted with chloroform, dried and the solvent removed. The acid was recrystallized from a suitable solvent.

General procedure for preparation of the methyl ester **7b**

The acid **7a** was dissolved in a minimal volume of ether and ethereal CH_2N_2 soln added until the yellow color persists. Removal of solvent and dissolution of the residue in a minimal volume of benzene followed by filtration through a column of neutral alumina (10 g per g ester), benzene as eluent, gave the ester **7b** after removal of solvent. The ester was then recrystallized.

General procedure for preparation of tetraenic imides, **6**

To a solution of dienic ester **7** (**b**, **c**, **e**, **f**, **i**, **j**, **k**, **l**; 1 mmol) in CCl_4 (25 ml) was added recryst NBS (2 mmol) and several grains of dibenzoyl peroxide. After ca 20 min succinimide floats on the solvent surface. After cooling, filtration and removal of solvent the crude dibromide is dissolved in dry benzene or in dry DMF (20 ml), 1,5-diazabicyclo[4.3.0]non-5-ene (4 mmol) was added and the whole is heated at reflux (C_6H_6) or at 100° (DMF) for 8 hr under N_2.

After cooling and washing C_6H_6 soln with dil HCl, satd NaClaq and drying the C_6H_6 was removed. Alternatively, the DMF soln was added to ice water (200 ml) and the product extracted with ether (4 × 50 ml), the soln dried and the solvent removed. The residue in either case was then filtered in C_6H_6 soln through a column of neutral alumina and chromatographed on prep silica plates.

General procedure for Diels–Alder reaction of **6**

To a soln of **6** in CH_2Cl_2 was added dropwise at r.t. or at temp of acetone-dry ice bath a soln of PTD in CH_2Cl_2. For prep of mono-adduct the disappearance of red color after 1eq PTD has been added is criterion for the end point. For prep of *bis*-adduct the persistence of red color after addition of 2 eq PTD is the criterion. The solvent was removed and products separated on prep silica plates and purified by recrystallization.

Photochemical cyclization to afford cage compounds, **10**

The *bis*-adduct **9** (30 mg) was dissolved in acetone (30 ml) and the tubes after 4 degas cycles through freezing and melting at 10^{-3} nm were irradiated in a Rayonet chamber at 300 nm overnight. When tlc showed the absence of **9**, as is usually the case, the solvent was removed and **10** purified by crystallization.

Methyl 11,13-dioxo-12-aza[4.4.3]*propella-3,8-diene-12-acetate*, **7b**

The free acid was prepared by method (b) above at 190°, m.p. 169–170° (hexane). Methylation with CH_2N_2 as above gave **7b**, m.p. 98–99° (CH_2Cl_2–hexane) in 70% yield from **2**. (Found: C, 65.39; H, 6.17; N, 5.15; M.W. 275.1147. $C_{15}H_{17}NO_4$ requires: C, 65.44; H, 6.22; N, 5.09%; M.W. 275.1157). IR: 2980–2500, 1780, 1720, 1400, 1100 cm^{-1}. NMR: 4.0 (m, 4 vinylic H); 5.8 (s, 2 H, C$\underline{H}_2$N); 6.3 (s, 3 H, $CO_2C\underline{H}_3$); 6.8–7.9 (m, 8 allylic H). MS: *m/e* M$^+$, 275 (35); 244 (5); 221 (50); 216 (10); 215 (19); 189 (10); 161 (100); 132 (14).

Methyl 11,13-dioxo-12-aza[4.4.3]*propella-2,4,7,9-tetraene-12-acetate*, **6b**

Prepared using DMF in 43% yield, m.p. 112–114° (CH_2Cl_2–hexane). (Found: M.W. 271.0859. $C_{15}H_{13}NO_4$ requires: M.W. 271.0845). IR: 2950, 1780, 1740, 1400 cm^{-1}. NMR: 3.8–4.5 (A_2B_2, 8 vinylic H); 5.67 (s, 2 H, C$\underline{H}_2$N); 6.25 (s, 3 H, $CO_2C\underline{H}_3$). MS: M$^+$, 271 (9); 240 (4); 212 (4); 129 (17); 128 (100).

Reaction of **6b** *with PTD*

(a) Tetraene (55 mg in 2 ml) gave immediate reaction with PTD (25 mg; 0.7 eq in 2 ml). Evaporation of CH_2Cl_2 gave recovered **6b** (14 mg) and mono-adduct **8b** (50 mg; 74 %) after recrystallization, m.p. 233° (CH_2Cl_2–hexane). (Found: C, 60.94; H, 4.13; N, 12.88. $C_{23}H_{18}N_4O_6$ requires C, 61.88; H, 4.06; N, 12.55 %). IR (KBr): 1790, 1760, 1740, 1720, 1620, 1520, 1420 cm^{-1}. NMR: 2.59 (s, 5 arom H); 3.33 (m, 2 vinylic H); 4.06 (m, 4 dienic H); 4.68 (m, 2 allylic H); 5.62 (s, 2 H, $C\underline{H}_2N$); 6.26 (s, 3 H, $CO_2C\underline{H}_3$). MS: 228 (10); 227 (100); 160 (16); 119 (37).

(b) The *bis*-adduct was formed from **8b** (84 mg in 2 ml) and PTD (35 mg in 2 ml) immediately. The product **9b** (75 mg; 64 %) after crystallization had m.p. 315–316° (CH_2Cl_2–hexane). (Found: N, 15.45; M.W. 621.1586. $C_{31}H_{23}N_7O_8$ requires: N, 15.77 %; M.W. 621.1607). IR: 1750 (br), 1400 cm^{-1}. NMR: 2.61 (s, 10 arom H); 3.71 (m, 4 vinylic H); 4.62 (m, 4 allylic H); 5.59 (s, 2 H, $C\underline{H}_2N$); 6.30 (s, 3 H, $CO_2C\underline{H}_3$). MS: M^+, 621 (1); 228 (6); 227 (54); 160 (64); 119 (57); 69 (100).

Photochemical cyclization of **9b** gave **10b** (78 %), m.p. > 320° (CH_2Cl_2–hexane). (Found: M.W. 621.1566). IR: 1750 (br) cm^{-1}. NMR 2.53 (s, 10 arom H); 4.90 (m, 4 H), $C\underline{H}N$); 5.57 (s, 2 H, $C\underline{H}_2N$); 6.33 (s, 3 H, $CO_2C\underline{H}_3$); 6.57 (m, 4 cyclobutane H). MS: M^+, 621 (14); 228 (6); 227 (19); 69 (100).

Preparation and reactions of 7c

A mixture of **7a** (4.6 g), thuonyl chloride (2.6 g) and dry benzene (50 ml) was heated under reflux and N_2 until reaction was complete. The solvent was removed and to the residue were added, n-hexanol (3 g), triethylamine (6 ml) and dry benzene (50 ml). The whole was stirred at r.t. for 48 hr, the solvent removed and the residue in benzene filtered through neutral alumina (20 g). Removal of solvent and distillation gave oily **7c** (1.8 g; 30 %), b.p. 150°/0.15 mm. (Found: C, 69.26; H, 8.11; N, 3.87, M.W. 345.1951. $C_{20}H_{27}NO_4$ requires: C, 69.54; H, 7.88; N, 4.06 %; M.W. 345.1940). IR: 3000–2800, 1780, 1760, 1720, 1500–1300, 1000 cm^{-1}. NMR: 4.0–4.2 (m, 4 vinylic H); 5.8 (s, 2 H, $C\underline{H}_2N$); 5.9 (t, 2 H, $CO_2C\underline{H}_2$; J = 6 Hz); 7.0–8.2 (m, 8 allylic H); 8.3–9.2 (m, 11 aliphatic H). M.S.: M^+, 345 (45); 291 (42); 261 (33); 243 (30); 169 (30); 162 (19); 161 (91); 149 (14); 131 (100).

n-*Hexyl* 11,13-*dioxo*-12-*aza*[4.4.3]*propella*-2,4,7,9-*tetraene*-12-*acetate*, **6c**

Prepared using C_6H_6 in dehydrobromination step in 43 % yield, b.p. 140°/0.1 mm. (Found: C, 69.70; H, 6.90; N, 3.92, $C_{20}H_{23}NO_4$ requires: C, 70.36; H, 6.79; N, 4.10 %). IR: 3000–2850, 1780, 1760, 1620, 1400 cm^{-1}. NMR: 3.9–4.5 (A_2B_2, 8 vinylic H); 5.7 (s, 2 H, $C\underline{H}_2N$); 5.9 (t, $2CO_2C\underline{H}_2$; J = 6 Hz); 8.2–9.2 (m, 11 aliph H). MS: 206 (11); 188 (8); 160 (41); 156 (10); 128 (100).

Reaction of **6c** *with PTD*

Immediate reaction occurred between **6c** (294 mg in 15 ml) and PTD (131 mg (0.87 eq) in 10 ml). After removal of solvent **6c** was recovered (45 mg) and mono-adduct **8c** (377 mg; 100 %) was obtained, m.p. 141° (CH_2Cl_2–hexane). (Found: C, 64.70; H, 5.44; N, 10.95. $C_{28}H_{28}N_4O_6$ requires: C, 65.10; H, 5.46; N, 10.85 %). IR: 1780, 1720 (br), 1400 cm^{-1}. NMR: 2.54 (s, 5 arom H); 3.33 (m, 2 vinylic H); 4.07 (m, 4 dienic H); 4.70 (m, 2 allylic H); 5.70 (s, 2 H, $C\underline{H}_2N$); 5.87 (t, 2 H, CO_2CH_2; J = 6 Hz); 8.2–9.2 (m, 11 aliph H). MS: 227 (100); 206 (20); 188 (10); 161 (23); 160 (73); 119 (48).

Bis-*adduct* **12c**

Mono-adduct **8c** (76 mg in 5 ml) was treated with PTD (26 mg in 2 ml) for 5 min. Removal of solvent gave **9c** (96 mg; 94 %), m.p. 227° (CH_2Cl_2-hexane). (Found: N, 13.79. $C_{36}H_{33}N_7O_8$ requires: N, 14.18 %). IR (KBr): 2950, 1750 (br), 1520, 1420, 1230 cm^{-1}. NMR: 2.61 (s, 10 arom H); 3.71 (m, 4 vinylic H); 4.63 (m, 4 allylic H); 5.63 (s, 2 H, $C\underline{H}_2N$); 5.90 (t, 2 H, $CO_2C\underline{H}_2$; J = 6 Hz); 8.2–9.2 (m, 11 aliph H). MS: 227 (51); 206 (15); 161 (17); 160 (53); 119 (100).

Photochemical cyclization of **9c** gave **10** (95 %), m.p. 213° (CH_2Cl_2–hexane). (Found: N, 13.94, M.W. 691.2432. $C_{36}H_{33}N_7O_8$ requires N, 14.18 %; M.W. 691.2390). IR (KBr): 2950, 1760–1720, 1600, 1500, 1420, 1200, 750 cm^{-1}. NMR: 2.55 (s, 10 arom H); 4.92 (m, 4 bridgehead H); 5.60 (s, 2 H, $C\underline{H}_2N$); 5.91 (t, 2 H, $CO_2C\underline{H}_2$); 6.57 (m, 4 cyclobutane H); 8.2–9.2 (m, 11 aliph H). MS: M^+, 691 (20); 227 (17); 183 (12); 133 (28); 119 (20); 101 (100).

Methyl 11′,13′-*dioxo*-12′-*aza*[4.4.3]*propella*-3′,8′-*diene*-12′-(2S)-*propionate*, **7e**

The acid **7d** was prepared by procedure (b) above at 190° in 58 % yield, m.p. 102–103° (CH_2Cl_2–hexane). The ester was prepared as above in 95 % yield, $[\alpha]_D = +0.62°$, m.p. 85–86° (CH_2Cl_2–hexane). (Found: C, 66.46; H, 6.57; N, 4.80; M.W. 289.1147. $C_{16}H_{19}NO_4$ requires: C, 66.42; H, 6.62; N, 4.84 %; M.W. 289.1313). IR: 2960–2840, 1780, 1760, 1720, 1420 cm^{-1}. NMR: 3.9–4.2 (m, 4 vinylic H); 5.26 (q, 1 H, $C\underline{H}N$; J = 8 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 7.0–8.1 (m, 8 allylic H); 8.53 (d, 3 H, $CHC\underline{H}_3$; J = 8 Hz). MS: M^+, 289 (8); 235 (5); 230 (4); 229 (8); 175 (14); 131 (13); 69 (100). Heating of **7e** in a sealed NMR tube at 90° for 19 hr did not cause apparent decomposition.

Methyl 11′,13′-[*a* *dioxo*-12′-*aza*-4.4.3]-*propella*-2′,4′,7′,9′-*tetraene*-12′-(2S)-*propionate*, **6e**

Prepared using DMF in 33 % yield, b.p. 115°/0.1 mm. (Found: C, 67.21; H, 5.36; N, 5.09; M.W. 285.0968. $C_{16}H_{15}NO_4$ requires: C, 67.36; H, 5.30; N, 4.91 %; M.W. 285.1000). IR: 2950, 1780, 1760, 1720, 1380, 1030 cm^{-1}. NMR: 3.8–4.5 (A_2B_2, 8 vinylic H); 5.17 (q, 1 H, $C\underline{H}N$); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 8.42 (d, 3 H, $CHC\underline{H}_3$; J = 8 Hz). MS: M^+, 285 (8), 254 (4); 226 (5), 174 (15); 129 (66); 127 (22); 69 (100).

Reaction of **6e** *with PTD*

(a) *At room temp.* Immediate reaction took place between **6e** (198 mg in 10 ml) with PTD (115 mg; 0.95 eq in 5 ml). Removal of solvent gave recovered **6e** (27 mg), mono-adduct **11e** (36 mg; 20 %), mono-adduct **8e** (141 mg; 51 %), *bis*-adduct **12e** (30 mg; 8 %) and *bis*-adduct **9e** (56 mg; 15 %).

Mono-adduct **11e** had m.p. 129–131° (CH_2Cl_2–hexane). (Found: N, 11.77. $C_{24}H_{20}N_4O_6$ requires: N, 12.17 %). IR (KBr): 3000–2900, 1800–1700, 1620, 1500, 1400, 1250 cm^{-1}. NMR: 2.57 (s, 5 arom H); 3.43 (m, 2 vinylic H); 3.30–4.0 (A_2B_2, 4 dienic H); 4.37 (m, 2 allylic H); 5.27 (q, 1 H, $C\underline{H}N$, J = 8 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 8.47 (d, 3 H, $CHC\underline{H}_3$; J = 8 Hz). MS: 227 (4), 174 (27), 130 (6), 119 (30); 69 (100).

Mono-adduct **8e** had m.p. 215° (CH_2Cl_2-hexane). (Found: N, 11,74 %). IR (KBr): 2950, 1800, 1750, 1730, 1410, 1240 cm^{-1}. NMR: 2.60 (s, 5 arom H); 3.37 (m, 2 vinylic H); 3.8–4.3 (m, 4 dienic H); 4.74 (m, 2 allylic H); 5.13 (q, 1 H, $C\underline{H}N$; J = 8 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 8.42 (d, 3 H, $CHC\underline{H}_3$; J = 8 Hz). MS: 227 (91); 174 (7); 130 (7); 119 (26); 43 (100).

(b) At −78°: Immediate reaction occurred between **6e** (230 mg in 5 ml) and PTD (75 mg; 0.53 eq in 5 ml). After removal of solvent **6e** (98 mg) was recovered and only *syn*-mono-adduct **8e** (183 mg; 86 %) was obtained. No traces of **11e** could be found by tlc.

Bis-*adduct* **12e**. Is best obtained by reacting **11e** (25 mg in 5 ml) with PTD (10 mg in 2 ml) in immediate reaction. Removal of solvent afforded **12e** (30 mg; 87 %), m.p. 190° (dec CH_2Cl_2–hexane). (Found: C, 59.74; H, 4.19; N, 14.63; M.W.: 635.1824. $C_{32}H_{25}N_7O_8$ requires: C, 60.47; H, 3.96; N, 15.43 %, M.W. 635.1764). IR (KBr): 2950, 1740 (br), 1610, 1510, 1400, 1250 cm^{-1}. NMR: 2.59 (s, 10 arom H); 3.45 (m, 4 vinylic H); 4.49 (m, 2 allylic H); 4.73 (t, 2 allylic H); 5.26 (q, 1 H, $C\underline{H}N$; J = 8 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$). MS: M^+, 635 (2); 227 (8); 174 (3); 119 (5); 69 (100).

Bis-adduct **9e** is best obtained by reacting **8e** (28 mg in 2 ml) with PTD until obtention of stable red color. Tlc showed presence of **9e** only obtained (35 mg; 90%) after removal of solvent, m.p. > 320° (acetone). (Found: C, 60.04; H, 4.23; N, 14.55%). IR (KBr): 2950, 1740 (br), 1510, 1400 cm^{-1}. NMR: 2.60 (s, 10 arom H); 3.7 (m, 4 vinylic H); 4.6 (m, 4 allylic H); 5.25 (q, 1 H, $C\underline{H}N$); 6.31 (s, 3 H, $CO_2C\underline{H}_3$). NMR spectrum calculated for A_2B_2 system: 3.7 (4 vinylic H of type B) 4.63 (4 allylic H of type A). $J_{AB} = J_{A'B'} = 5.8$ Hz; $J_{BB'} = 10$ Hz; $J_{A'B} = J_{AB'} = 1.8$ Hz; $J_{AA'} = 0$. MS: 227 (43); 174 (100); 147 (14), 130 (15), 119 (50).

Photochemical cyclization of **9e** gave **10e** in 92% yield, m.p. > 320° (acetone). (Found: C, 59.55; H, 4.15; N, 14.91%; M.W. 635.1741). IR (KBr): 2960, 1780, 1750, 1720, 1620, 1500, 1400, 770 cm^{-1}. NMR: 2.49 (s, 10 arom H); 4.90 (m, 4 bridgehead H); 6.44 (s, 3 H, $CO_2C\underline{H}_3$); 6.57 (m, 4 cyclobutane H). MS: M$^+$, 635 (78); 227 (100); 119 (37).

t-*Butyl* 11′,13′-*dioxo*-12′-*aza*[4.4.3]*propella*-3′,8′-*diene*-12′-(2S)-*propionate*, **7f**

This ester was prepared from **7d** (4.5 g), t-BuOH (5 ml), *p*-tosyl chloride (6.5 g) and triethylamine (30 ml) by heating under reflux for 15 hr. The solvent was removed, the residue taken up in C_6H_6 and washed with 5% KOH aq. The benzene soln was filtered through a column of neutral alumina. Removal of solvent and distillation gave **7f** (3.3 g, 60%), b.p. 200°/1 mm, $[\alpha]_D = -0.18°$. (Found: N, 4.55. $C_{19}H_{25}NO_4$ requires: N, 4.25%). IR: 3000–2800, 1780, 1750, 1700, 1400. 1150 cm^{-1}. NMR: 4.0–4.2 (m, 4 vinylic H); 5.4 (q, 1 H, $C\underline{H}N$; J = 11 Hz); 7.1–8.1 (m, 8 allylic H); 8.6 (s, 9 H, $C(C\underline{H}_3)_3$); 8.7 (d, 3H. $CHC\underline{H}_3$) MS: 275 (39); 258 (8); 231 (22); 230 (50); 229 (21); 175 (17); 131 (36); 105 (10); 51 (100).

t-*Butyl* 11′,12′-*dioxo*-12′-*aza*-[4.4.3]-*propella*-2′,4′,7′,9′-*tetraene*-12′-(2S)-*propionate*, **6f**

Prepared using benzene in 35% yield as an oil, b.p. 180°/0.1 mm. (Found: N, 4.07; N.W. 327.1441. $C_{19}H_{21}NO_4$ requires: N, 4.28%; M.W. 327.1470). IR: 2950, 1780, 1740, 1710, 1380, 1150 cm^{-1}. NMR: 3.9–4.5 (A_2B_2, 8 vinylic H); 5.2 (q, 1 H, $C\underline{H}N$; J = 11 Hz); 8.6 (s, 9 H, $C(C\underline{H}_3)_3$); 8.6 (d, 3 H, $CHC\underline{H}_3$). MS: M$^+$, 327 (2); 227 (6); 212 (15); 205 (14); 155 (11); 129 (22); 128 (100); 127 (18).

Reaction of **6f** *with PTD*

(a) At *room temp.* Reaction between **6f** (230 mg in 10 ml) with PTD (310 mg in 10 ml) was at first rapid but slow towards end of addition of PTD. Removal of solvent gave **12f** (194 mg; 41%) and **9f** (161 mg; 34%).

Bis-adduct **12f** had m.p. 188° (dec, CH_2Cl_2-hexane). (Found: M.W. 677.2246. $C_{35}H_{31}N_7O_8$ (peak matching) requires: M.W. 677.2234). IR (KBr): 2900, 1780, 1750, 1730, 1600, 1500, 1400 cm^{-1}. NMR: 2.5 (s, 10 arom H); 3.2–3.6 (m, 4 vinylic H); 4.3–4.6 (m, 4 allylic H); 5.2 (q, 1 H, $C\underline{H}N$); 8.6 (s, 9 H, $C(C\underline{H}_3)_3$); 8.7 (d, 3 H, $CHC\underline{H}_3$). MS: 231 (21); 227 (19); 183 (15); 174 (14); 169 (23); 165 (17); 133 (31); 119 (100).

Bis-adduct **9f** had m.p. 298–300° (CH_2Cl_2–hexane). (Found: N, 14.59. $C_{35}H_{31}N_7O_8$ requires: N, 14.47%). IR (KBr): 2900, 1780, 1740 (br); 1500, 1400 cm^{-1}. NMR: 2.6 (s, 10 arom H); 3.5–3.8 (m, 4 vinylic H); 4.5–4.8 (m, 4 allylic H); 5.2 (q, 1 H, $C\underline{H}N$); 8.5 (d, 3 H, $CHC\underline{H}_3$); 8.6 (s, 9 H, $C(C\underline{H}_3)_3$). MS: 227 (40), 174 (16); 119 (28); 70 (100).

(b) *At* −78°. The reaction between **6f** (175 mg in 10 ml) with PTD (200 mg in 10 ml) was rapid, then slow. After removal of solvent **12f** (200 mg; 55%) and **9f** (143 mg; 39%) were obtained.

Photochemical cyclization of **9f** gave **10f** in 80% yield, m.p. > 320° (CH_2Cl_2–hexane). (Found: M.W. 677.3240). IR (KBr): 2900, 1780, 1720 (br), 1400 cm^{-1}. NMR: 2.5 (s, 10 arom H); 4.7–5.0 (m, 4 bridgehead H); 8.7 (s, 9 H, $C(C\underline{H}_3)_3$); 8.7 (d, 3 H, $CHC\underline{H}_3$). MS: M$^+$, 677 (13); 576 (11); 227 (100); 119 (44).

Methyl 11′,13′-*dioxo*-12′-*aza*[4.4.3]*propella*-3′,8′-*diene*-12′-2,2-*methyl-propionate*, **13b**

The acid was prepared by route (a) above, melting using a flame for 30 min in 95% yield, m.p. 154–155° (benzene). The ester was prepared as usual in 95% yield, m.p. 100–101° (CH_2Cl_2–hexane). (Found: N, 4.17; M.W. 303.1426. $C_{17}H_{21}NO_4$ requires: N, 4.62%; M.W. 303.1470). IR (KBr): 2900, 1760, 1720, 1380, 1250 cm^{-1}. NMR: 4.0–4.3 (m, 4 vinylic H); 6.33 (s, 3 H, $CO_2C\underline{H}_3$); 7.2–8.2 (m, 8 allylic H); 8.39 (s, 6 H, CH_3). MS: M$^+$, 303 (3); 271 (13); 244 (9); 243 (13); 190 (17).

Methyl 11′,13′-*dioxo*-12′-*aza*[4.4.3]-*propella*-2′,4′,7′,9′-*tetraene*-12′-2,2-*methyl-proprionate*, **14b**

The ester was prepared using DMF, in 28% yield, m.p. 77–78° (CH_2Cl_2–hexane). (Found: N, 4.11; M.W. 299.1169. $C_{17}H_{17}NO_4$ requires: N, 4.68%; M.W. 299.1158). IR (KBr): 2900, 1780, 1760, 1720, 1660, 1340 cm^{-1}. NMR: 3.8–4.6 (A_2B_2, 8 vinylic H); 6.31 (s, 3 H, $CO_2C\underline{H}_3$); 8.29 (s, 6 H, $C\underline{H}_3$). MS: M$^+$, 299 (3); 240 (4); 188 (4); 129 (15); 128 (100).

Reaction of **14b** *with PTD*

(a) *At room temp.* Immediate reaction occurred with **14b** (145 mg in 5 ml) and PTD (80 mg; 0.94 eq in 5 ml). After removal of solvent **14b** (16 mg) was recovered with mono-adduct **15** (170 mg; 82%) and *bis*-adduct **17** (17 mg; 6%).

Mono-adduct **15** had m.p. 179–180° (CH_2Cl_2–hexane). (Found: N, 11.43. $C_{25}H_{22}N_4O_6$ requires: N, 11.81%). IR (KBr): 2900, 1750 (br), 1500, 1400, 1340, 1230 cm^{-1}. NMR: 2.60 (s, 5 arom H); 4.40 (m, 2 vinylic H); 4.15 (m, 4 dienic H); 4.80 (m, 2 allylic H); 6.31 (s, 3 H, $CO_2C\underline{H}_3$); 8.27 (s, 6 H, $C\underline{H}_3$). MS: 227 (100); 188 (51); 148 (21); 130 (27); 119 (79).

(b) *At* −78°. **14b** and PTD gave 1:1 mixture of *bis*-adducts **17** and **16**.

Bis-adducts were best prepared from **15** (45 mg in 5 ml) and PTD (17 mg in 2 ml) during 3 min. After removal of solvent **16** (20 mg; 32%) and **17** (27 mg; 44%) were isolated.

Bis-adduct **16** had m.p. 237–238° (CH_2Cl_2–hexane). (Found: M.W. 649.1828. $C_{33}H_{27}N_7O_8$ requires: M.W. 649.1910). IR (KBr): 2900, 1780, 1720 (br), 1610, 1500, 1400 cm^{-1}. NMR: 2.59 (s, 10 arom H); 3.43 (m, 4 vinylic H); 4.60 (m, 4 allylic H); 6.32 (s, 3 H, $CO_2C\underline{H}_3$), MS: M$^+$, 649 (1); 227 (33); 188 (100), 177 (17); 148 (82); 119 (100).

Bis-adduct **17** had m.p. 270° (dec, CH_2Cl_2–hexane). (Found: M.W. 649.1914). IR (KBr): 2900, 1780, 1730 (br), 1600, 1500, 1400 cm^{-1}. NMR: 2.60 (s, 10 arom H); 3.72 (m, 4 vinylic H); 4.69 (m, 4 allylic H); 6.33 (s, 3 H, $CO_2C\underline{H}_3$); 8.23 (s, 6 H, $C\underline{H}_3$). MS: M$^+$, 649 (1); 227 (40); 188 (15); 119 (20); 70 (100).

Photochemical cyclization of **17** gave **18** in 79% yield, m.p. 283–284° (benzene). (Found: N, 14.75; M.W. 649.1940. $C_{33}H_{27}N_7O_8$ requires: N, 15.09%; M.W. 649.1921). IR (KBr): 2880, 1750 (br), 1500, 1400, 1300, 1250 cm^{-1}. NMR: 2.51 (s, 10 arom H); 4.97 (m, 4 bridgehead H); 6.60 (m, 3 H, $CO_2C\underline{H}_3$ + 4 cyclobutane H); 8.23 (s, 6 H, $C\underline{H}_3$). Irradiation at τ 4.97 gave 6.59 (s, 3 H, $CO_2C\underline{H}_3$); 6.64 (m, 4 cyclobutane H). MS: M$^+$, 649 (21); 227 (36); 119 (27); 69 (100).

Methyl 11′,13′-*dioxo*-12′-*aza*[4.4.3]*propella*-3′,8′-*diene*-12-1-*cyclopentanoate* **13d**

1-Aminocyclopentane-1-carboxylic acid was prepared according to Adkins and Billica,[6] in 42% yield. Its methyl ester was prepared by Fischer esterification in dry methanol with dry HCl gas, in 80% yield.

The free acid **13c** was prepared by route (b) above, at 250°, in 73% yield, m.p. 142–143° (CH_2Cl_2–hexane). The methyl ester **13d** was prepared as usual with CH_2N_2 in 93% yield, m.p. 65–66° (CH_2Cl_2–hexane). (Found: N, 4.09; M.W. 329.1637. $C_{19}H_{23}NO_4$ requires: N, 4.25%; M.W. 329.1627). IR: 2900, 1800, 1720 cm^{-1}. NMR: 4.0–4.4 (m, 4 vinylic H); 6.4 (s, 3 H, $CO_2C\underline{H}_3$); 7.0–8.0 (m, 8 allylic + 8 alicyclic H). MS: M$^+$, 329 (19); 270 (75); 215 (48); 214 (40); 204 (79); 131 (77); 130 (23); 129 (24); 117 (77); 69 (100).

13c may also be prepared azeotropically by route (a) from **2** and methyl 1-aminocyclopentanoate.

Methyl 11′13′-dioxo-12′-aza-[4.4.3]-*propella-2′,4′,7′,9′-tetraene-12′-1-cyclopentanoute*, 19

This was prepared using DMF in 26% yield, m.p. 102–103° (CH_2Cl_2-hexane). (Found: N, 4.16. $C_{19}H_{19}NO_4$ requires: N, 4.31%). IR (KBr): 2900, 1790, 1740, 1700, 1450 cm^{-1}. NMR: 3.8–4.6 (A_2B_2, 8 vinylic H); 4.3 (s, 3 H, $CO_2C\underline{H}_3$); 7.4–8.7 (m, 8 alicyclic H). NMR calculated for A_2B_2 system: $J_{AA'}$ = 1 Hz; $J_{AB'}$ = 0.7 Hz; J_{AB} = 9.5 Hz; $J_{BB'}$ = 4.5 Hz; $\Delta\delta_{AB}$ = 25 Hz. MS: 266 (3); 129 (16); 128 (100); 127 (4).

Reaction of 19 *with PTD*

(a) *At room temp.* Immediate reaction took place between **19** (93 mg in 5 ml) and PTD (45 mg; 0.9 eq in 5 ml). Removal of solvent gave recovered **9** (19 mg), mono-adduct **20** (19 mg; 17%), mono-adduct **21** (71 mg; 62%) and *bis*-adduct **22** (5 mg; 3%).

Mono-adduct **20** had m.p. 158–159° (CH_2Cl_2–hexane). IR (KBr): 2900, 1790, 1760, 1720, 1400 cm^{-1}. NMR: 2.6 (s, 5 arom H); 3.45 (m, 2 vinylic H); 3.5–4.3 (A_2B_2, 4 dienic H); 4.6 (m, 2 allylic H); 6.33 (s, 3 H, $CO_2C\underline{H}_3$); 7.4–8.5 (m, 8 alicyclic H). MS: 227 (84); 214 (100); 178 (8); 148 (97); 130 (49); 119 (32).

Mono-adduct **21** had m.p. 193° (CH_2Cl_2-hexane). (Found: N, 11.10. $C_{27}H_{24}N_4O_6$ requires: N, 11.19%). IR (KBr): 2900, 1790, 1730 (br), 1400 cm^{-1}. NMR: 2.6 (s, 5 arom H); 3.4 (m, 2 vinylic H); 4.0 (m, 4 dienic H); 4.7 (m, 2 allylic H); 6.3 (s, 3 H, $CO_2C\underline{H}_3$); 7.2–8.3 (m, 8 alicyclic H). MS: 228 (100), 227 (10); 214 (4); 148 (23); 128 (10); 119 (45).

Bis-adduct **22** was best prepared from **20** (6 mg in 3 ml) with solid PTD until red color persisted. Removal of solvent gave **22**, m.p. 230° (dec, CH_2Cl_2–hexane). (Found: M.W. 675.2178. $C_{35}H_{29}N_7O_8$ requires M.W. 675.2077). IR (KBr): 2900, 1790, 1730 (br), 1500, 1400 cm^{-1}. NMR: 2.6 (s, 10 arom H); 3.3–3.6 (m, 4 vinylic H); 4.4–4.8 (m, 4 allylic H); 6.3 (s, 3 H, $CO_2C\underline{H}_3$); 7.3–8.5 (m, 8 alicyclic H). MS: M$^+$, 675 (10); 233 (14); 227 (74); 213 (19); 212 (22); 201 (19); 189 (36); 133 (27); 119 (27).

Bis-adduct **23** was prepared from **21** (16 mg in 3 ml) and PTD (6 mg in 2 ml) during 5 min. After removal of solvent crystallization gave **23** (20 mg; 94%), m.p. 277° (CH_2Cl_2-hexane). (Found: N, 13.91, M.W. +1, 676.2131. $C_{35}H_{29}N_7O_8$ requires: N, 14.50%; M.W. 675.2111. IR (KBr): 2900, 1790, 1740 (br), 1500, 1400 cm^{-1}. NMR: 2.60 (s, 10 arom H); 3.72 (m, 4 vinylic H); 4.67 (m, 4 allylic H); 6.33 (s, 3 H, $CO_2C\underline{H}_3$); 7.0–8.4 (m, 8 alicyclic H). MS: M$^+$ + 1, 676 (1); M$^+$, 675 (1); 227 (100); 214 (46); 148 (55); 130 (19); 119 (80).

(b) *At* −78°: Immediate reaction took place between **19** (83 mg in 10 ml) and PTD (90 mg in 5 ml). After removal of solvent an upper fraction was isolated containing **22**:**23** in a ratio of 1:2 (NMR), i.e. 3% and 6% respectively and a second fraction of **23** (156 mg; 90%).

Photochemical cyclization of **23** gave **24** in 88% yield, m.p. > 320° (CH_2Cl_2–hexane). (Found: N, 13.79; M.W. 675.2027). IR (KBr): 2900, 1740 (br), 1500, 1400 cm^{-1}. NMR: 2.5 (s, 10 arom H); 4.9 (m, 4 bridgehead H); 6.5 (s, 3 H, $CO_2C\underline{H}_3$); 6.6 (m, 4 cyclobutane H); 7.0–8.5 (m, 8 cyclopentane H). MS: M$^+$, 675 (3); 319 (100); 317 (17); 312 (13); 305 (31); 301 (20); 233 (16); 183 (25); 133 (31).

Dimethyl 11′,13′-dioxo-12′-aza[4.4.3]*propella-3′,8′-diene-12′-*(2S)*-succinate*, 7g

Dimethyl aspartate hydrochloride (4.5 g) was dissolved in MeOH (10 ml) and titrated to neutral pH with 10% methanolic KOH. After removal of solvent the residue was dissolved in toluene and the insoluble salt removed by filtration. To the filtrate was added **2** (4 g) and triethylamine (3 ml). The whole was heated under reflux overnight, cooled and solvent removed. After chromatography on silica, then neutral alumina the product (3 g; 44%) had b.p. 100°/0.01 mm, $[\alpha]_D$ = −2.64°. (Found: M.W. 347.1364. $C_{18}H_{21}NO_6$ requires: M.W. 347.1368). IR: 2900, 1790, 1750, 1720, 1400 cm^{-1}. NMR: 4.0–4.2 (m, 4 vinylic H); 5.2 (dd, 1 H, $C\underline{H}N$, J = 20 Hz); 6.3 (2s, 6 H, $CO_2C\underline{H}_3$); 6.9 (m, 2 H, $C\underline{H}_2CO_2$); 7.0–8.2 (m, 8 allylic H). MS: M$^+$, 347 (19); 315 (18); 293 (12); 288 (12); 287 (28); 255 (23); 233 (31); 201 (29); 131 (100); 129 (26).

Dimethyl 11′,13′-dioxo-12′-aza[4.4.3]*propella-2′,4′,7′,9′-tetraene-12′-*(2S)*-succinate*, 6g

Prepared using benzene in 41% yield, b.p. 110°/0.01 mm. (Found: N, 3.95. M.W. 343.1036. $C_{18}H_{27}NO_6$ requires: N, 4.08%; M.W. 343.1056). IR: 2950, 1790, 1750, 1720, 1400 cm^{-1}. NMR: 3.9–4.5 (A_2B_2, 8 vinylic H); 4.65 (dd, 1 H, $C\underline{H}N$; J = 16 Hz); 6.25 (s, 3 H, $CO_2C\underline{H}_3$); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 6.8 (m, 2 H, $C\underline{H}_2CO_2$). MS; M$^+$, 343 (3); 284 (4); 258 (4); 232 (8); 200 (17); 130 (10); 128 (100).

Reactions of 6g *with PTD*

(a) *At room temp.* Immediate reaction occurred between **6g** (267 mg in 10 ml) and PTD (115 mg; 0.84 eq in 5 ml). After removal of solvent **6g** (71 mg) was recovered then fraction of monoadduct **11g** (5 mg; 2%), mono-adduct **8g** (147 mg; 48%), a difficulty separable mixture of **11g** and **8g** (74 mg) estimated by NMR to be composed of **11g** (17%; 48 mg) and **8g** (8%; 25 mg). Finally, *bis*-adduct **12g** (25 mg; 6%) was isolated.

Mono-adduct **11g** had IR: 2950, 1730 (br), 1350 cm^{-1}. NMR: 2.6 (s, 5 arom H); 3.52 (m, 2 vinylic H); 3.6–4.3 (A_2B_2, 4 dienic H), 4.78 (m, 2 allylic H + 1 H, $C\underline{H}N$); 6.28 (s, 3 H, $CO_2C\underline{H}_3$); 6.36 (s, 3 H, $CO_2C\underline{H}_3$); 6.8 (m, 2 H, $C\underline{H}_2CO_2$). MS 259 (22); 232 (84); 227 (31); 200 (100); 190 (40); 172 (11); 130 (37); 119 (49).

Mono-adduct **8g** had m.p. 241–242° (dec, CH_2Cl_2–hexane). (Found: N, 11.03. $C_{26}H_{22}N_4O_8$ requires N, 11.11%). IR (KBr): 3000, 1790, 1750 (br), 1500, 1400 1280 cm^{-1}. NMR: 2.6 (s, 5 arom H); 3.4 (m, 2 vinylic H); 4.1 (m, 4 dienic H); 4.8 (m, 2 allylic H + 1 H, $C\underline{H}N$); 6.3 (s, 3 H, $CO_2C\underline{H}_3$); 6.4 (s, 3 H, $CO_2C\underline{H}_3$); 6.8 (m, 2 H, $C\underline{H}_2CO_2$). MS: 283 (100); 227 (44); 219 (15); 183 (10); 119 (37).

(b) *At* −78°: **6g** (71 mg in 5 ml) was reacted with PTD (25 mg; 0.69 eq in 3 ml) affording **6g** (17 mg), mono-adduct mixture (47 mg, by NMR 18% **11g** and 40% **8g**) and **8g** (33 mg 40%).

Bis-adduct **12g** was obtained by dissolving **11g** in an NMR tube and adding excess PTD. NMR and tlc showed that only **12g** is formed, m.p. 250° (dec, CH_2Cl_2–hexane). (Found: N, 13.62, M.W. 693.1974. $C_{34}H_{27}N_7O_{10}$ requires: N, 14.14% M.W. 693.1819). IR (KBr): 3000, 1750 (br), 1500, 1400 cm^{-1} NMR: 2.6 (s, 10 arom H); 3.5 (m, 4 vinylic H); 4.4–5.0 (m, 4 allylic H + 1 H, $C\underline{H}N$); 6.3 (s, 3 H, $CO_2C\underline{H}_3$); 6.5 (s, 3 H $CO_2C\underline{H}_3$); 6.9 (m, 2 H, $C\underline{H}_2CO_2$). MS: M$^+$, 693 (39); 25 (20); 232 (78); 227 (66); 200 (81); 190 (24); 130 (18); 119 (100)

Bis-adduct **9g** was prepared from **8g** (56 mg in 5 ml) an PTD (19 mg in 2 ml) during 5 min. The product crystallize from the mixture affording **9g** (69 mg; 92%), m.p. 275° (dec CH_2Cl_2). (Found: N, 13.57%). IR (KBr): 3000, 1780, 172 (br), 1500, 1400 cm^{-1}. NMR (CD_3CN at 42°): 2.48 (s, 1 arom H); 3.70 (m, 4 vinylic H); 4.66 (m, 4 allylic H). MS: 23 (12); 228 (17); 227 (100); 200 (15); 130 (8); 119 (61).

Photochemical cyclization of **9g** gave 10g in 87% yield m.p. > 320° (CH_2Cl_2–hexane). (Found: M.W. 693.1822). I (KBr): 2900, 1730 (br), 1400 cm^{-1}. NMR (CD_3CN at 50°C) 2.46 (s, 10 arom H); 4.60 (m, 1 H, $C\underline{H}N$); 5.00 (m, bridgehead H); 6.43 (s, 3 H, $CO_2C\underline{H}_3$); 6.52 (s, 3 H $CO_2C\underline{H}_3$); 6.64 (m, 4 cyclobutane H); 6.90 (m, 2 H $C\underline{H}_2CO_2$). MS: M$^+$, 693 (0.3); 520 (100); 227 (66); 212 (15) 193 (39); 146 (31); 132 (40); 119 (64).

Methyl 11′,13′-dioxo-12′-aza[4.4.3]*propella-3′,8′-diene-12′* (2S)*-4-methylpentanoate*, 7i

The free acid **7h** was prepared by the azeotropic metho using pyridine, m.p. 153–155° (CH_2Cl_2–hexane). The meth ester **7i** was prepared with CH_2N_2 as above in 70% yiel based on **2**, m.p. 97–99° (CH_2Cl_2–hexane), $[\alpha]_D$ = −1.21 (Found: C, 69.14; H, 7.79; N, 4.20. $C_{19}H_{25}NO_4$ require: C

68.86; H, 7.60; N, 4.23%). IR: 2920, 1800, 1760, 1730, 1400 cm^{-1}. NMR: 3.8-4.2 (m, 4 vinylic H); 5.3 (dd, 1 H, C$\underline{H}$N; J = 18 Hz); 6.2 (s, 3 H, $CO_2C\underline{H}_3$); 7.0–9.2 (m, 8 allylic + 9 aliphatic H). MS: 275 (100); 244 (25), 222 (22); 215 (62); 189 (27); 132 (42); 131 (26).

Methyl 11′,13′-dioxo-12′-aza-[4.4.3]-propella-2′,4′,7′,9′-tetraene-12′-(2S)-4-methylpentanoate, **6i**

Prepared using DMF in 33% yield, m.p. 86–88 (CH_2Cl_2–hexane). (Found: C, 69.64; H, 6.37; N, 4.34. $C_{19}H_{21}NO_4$ requires: C, 69.70; H, 6.47; N, 4.28%). IR: 2950, 1800, 1770, 1730, 1400, 1120 cm^{-1}. NMR: 3.8–4.4 (A_2B_2, 8 vinylic H); 5.13 (dd, 1 H, C$\underline{H}$N; J = 18 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 7.4–9.2 (m, 9 aliph H). MS: 271 (4); 130 (4); 128 (100).

Reaction of **6i** *with PTD*

(a) *At room temp.* Immediate reaction occurred between **6i** (124 mg in 5 ml) and PTD (60 mg; 0.9 eq in 2 ml). Removal of solvent gave recovered **6i** (26 mg), mono-adduct **11i** (67 mg; 45%) and mono-adduct **8i** (82 mg; 55%).

Mono-adduct **11i** had m.p. 148–149° (CH_2Cl_2–hexane). (Found: C, 63.86; H, 5.20. $C_{27}H_{26}N_4O_6$ requires C, 64.55; H, 5.22%). IR: 2950, 1720 (br), 1400, 1120 cm^{-1}. NMR: 2.53 (s, 5 arom H); 3.33 (m, 2 vinylic H); 3.6–4.3 (A_2B_2, 4 dienic H); 4.70 (m, 2 allylic H); 5.27 (dd, 1 H, C$\underline{H}$N; J = 18 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 7.8–9.2 (m, 9 aliph H). MS: 227 (70); 216 (55); 174 (35); 160 (100); 148 (20); 119 (41).

Mono-adduct **8i** had m.p. 210 211 (CH_2Cl_2 hexane). (Found: C, 63.91, H, 5.28). IR: 2950, 1780, 1730 (br), 1400, 1100 cm^{-1}. NMR: 2.53 (s, 5 arom H); 3.33 (m, 2 vinylic H); 4.07 (m, 4 dienic H); 4.70 (m, 2 allylic H); 5.10 (dd, 1 H, C$\underline{H}$N; J = 18 Hz); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 7.6–9.3 (m, 9 aliph H). MS: 227 (99); 128 (6); 119 (20); 69 (100).

(b) *At* −78°. Immediate reaction occurred between **11i** (30 mg in 2 ml) and PTD (11 mg in 2 ml). Evaporation of solvent gave *bis*-adduct **12i** (34 mg; 84%), m.p. 271–272° (CH_2Cl_2–hexane). (Found: C, 62.22; H, 5.07; M.W. 677.2218. $C_{35}H_{31}N_7O_8$ requires: C, 62.03; H, 4.61%; M.W. 677.2233). IR: 2900, 1800, 1750, 1400, 1100 cm^{-1}. NMR: 2.57 (s, 10 arom H); 3.47 (m, 4 vinylic H); 4.44 (m, 2 allylic H); 4.70 (m, 2 allylic H); 6.30 (s, 3 H, $CO_2C\underline{H}_3$); 7.8–9.2 (m, 9 aliph H). MS: M^+, 677 (9); 227 (74); 216 (51); 174 (24); 160 (76); 148 (12); 119 (10); 81 (100).

Bis-adduct **9i** was prepared in immediate reaction between **8i** (32 mg in 2 ml) and PTD (12 mg in 2 ml). Removal of solvent and trituration with $CHCl_3$ gave **9i** (35 mg; 81%), m.p. > 320°. (Found: M.W. 677.2222). IR (KBr): 2960, 1720 (br), 1500, 1410 cm^{-1}. NMR (DMSO-d_6): 2.51 (s, 10 arom H); 3.70 (m, 4 vinylic H); 4.50 (m, 4 allylic H). MS: M^+, 677 (5); 227 (100); 128 (6); 119 (3).

Photochemical cyclization of **9i** gave **10i** in 83% yield, m.p. > 345° (CH_2Cl_2–hexane). (Found: M.W. 677.2223). IR (KBr): 2900, 1780, 1750, 1420 cm^{-1}. NMR: 2.5 (s, 10 arom H); 4.9 (m, 4 bridgehead H); 6.4 (s, 3 H, $CO_2C\underline{H}_3$); 6.6 (m, 4 cyclobutane H). MS: M^+, 677 (68); 227 (89); 119 (39).

n-Hexyl 11′,13′-dioxo-12′aza[4.4.3]propella-3′,8′-diene-12′-(2S)-4-methylpentanoate **7j**

Azeotropic distillation overnight with a Dean-Stark condenser of a soln in benzene (200 ml) of the free acid **7h** (2.68 g), n-hexanol (1.4 g) and conc H_2SO_4 (1 ml) gave after cooling, washing with aq Na_2CO_3 (10%; 2 × 50 ml) and satd salt solution and removal of benzene, the ester **7j**, b.p. 150–155°/0.01 mm (2.04 g; 61%). (Found: C, 71.66; H, 8.51; N, 3.50; M.W. 401.2583. $C_{24}H_{35}NO_4$ requires: C, 71.79; H, 8.79; N, 3.49% M.W. 401.2565). IR. 2900, 1790, 1760, 1720, 1460. 1400, 1260 cm^{-1}. NMR: 3.8–4.2 (m, 4 vinylic H); 5.33 (dd, 1 H, C$\underline{H}$N; J = 16 Hz); 5.90 (t, 2 H, $CO_2C\underline{H}_2$; J = 7 Hz); 7.0–9.2 (m, 20 aliph H). MS: M^+, 401 (35); 347 (10); 299 (10); 272 (27); 271 (61); 217 (30); 204 (12); 119 (100).

n-Hexyl 11′,13′-dioxo-12′-aza[4.4.3]propella-2′,4′,7′,9′-tetraene-12′-(2S)-4-methylpentanoate **6j**

The tetraene was prepared using benzene, in 17% yield, b.p. 115°/0.01 mm. (Found: N, 3.28. $C_{24}H_{31}NO_4$ requires N, 3.52%). IR: 2900, 1790, 1750, 1720, 1660, 1380, 1250 cm^{-1}. NMR: 3.6–4.4 (A_2B_2, 8 vinylic H); 5.17 (dd, 1 H, C$\underline{H}$N, J = 18 Hz); 5.90 (t, 2 H, $CO_2C\underline{H}_2$, J = 6 Hz); 7.4–9.2 (m, 20 aliph H). MS: 341 (3); 289 (4); 160 (11); 129 (40); 128 (100).

Reaction of **6j** *with PTD*

(a) *At room temp.* Immediate reaction occurred between **6j** (126 mg in 5 ml) and PTD (45 mg; 0.81 eq in 5 ml). Removal of solvent afforded a mixture of mono-adduct **11j** (56 mg; 31%), mono-adduct **8j** (73 mg; 40%); *bis*-adduct **12j** (18 mg, 7%) and *bis*-adduct **9j** (3 mg; 1%).

Mono-adduct **11j** had m.p. 100–101° (CH_2Cl_2–hexane). (Found: N, 10.08. $C_{32}H_{36}N_4O_6$ requires: N, 9.78%). IR (KBr): 2900, 1730 (br), 1600, 1500, 1400, 1250 cm^{-1}. NMR: 2.57 (s, 5 arom H); 3.43 (m, 2 vinylic H); 3.5–4.2 (A_2B_2, 4 dienic H); 4.77 (m, 2 allylic H); 5.33 (dd, 1 H, C$\underline{H}$N; J = 18 Hz); 5.90 (t, 2 H, $CO_2C\underline{H}_2$, J = 6 Hz); 7.6–9.4 (m, 20 aliph H). MS: 282 (52); 227 (54); 216 (100); 160 (100); 119 (87).

Mono-adduct **8j** had m.p. 143–144 (CH_2Cl_2–hexane). (Found: C, 67.19; H, 6.34; N, 9.86. $C_{32}H_{36}N_4O_6$ requires: C, 67.11, H, 6.34; N, 9.78%). IR (KBr). 2900, 1790, 1740, 1600, 1400 cm^{-1}. NMR: 2.57 (s, 5 arom H); 3.33 (m, 2 vinylic H); 3.8–4.2 (m, 4 dienic H); 4.70 (m, 2 allylic H); 5.13 (dd, 1 H, C$\underline{H}$N, J = 15 Hz); 5.90 (t, 2 H, $CO_2C\underline{H}_2$, J = 6 Hz); 7.6–9.2 (m, 20 aliph H). MS: 281 (8); 227 (100); 161 (11); 119 (27).

(b) *At* −78°. **6j** (165 mg in 5 ml) reacted immediately with PTD (51 mg; 0.7 eq in 5 ml). Removal of solvent gave **6j** (50 mg), **11j** (54 mg; 32%); **8j** (107 mg; 64%); **12j** (4 mg; 3%) and **9j** (4 mg; 3%).

Bis-adduct **12j** is best prepared from **11j** (36 mg in 2 ml) with PTD (9 mg in 2 ml). Immediate reaction occurs. Solvent was removed and the product was crystallized from hexane (33 mg; 70%), m.p. 152–153° (CH_2Cl_2–hexane). IR (KBr): 2900, 1790, 1740 (br), 1600, 1500, 1400, 1250 cm^{-1}. NMR: 2.50 (s, 10 arom H); 3.2–3.6 (m, 4 vinylic H); 4.43 (m, 2 allylic H); 4.67 (m, 2 allylic H), 5.27 (dd, 1 H, C$\underline{H}$N); 5.87 (t, 2 H, $CO_2C\underline{H}_2$, J = 6 Hz); 7.4–9.4 (m, 20 aliph H). MS: 289 (24); 227 (35); 224 (22); 216 (65); 183 (20); 175 (20); 167 (87); 149 (100); 146 (75); 119 (52).

Bis-adduct **9j** prepared during 20 min reaction of **8j** (73 mg in 5 ml) with PTD (22 mg in 2 ml). Removal of solvent gave **9j** (87 mg; 91%), m.p. 275° (dec, CH_2Cl_2 -hexane). (Found: N, 12.40. $C_{40}H_{41}N_7O_8$ requires: N, 13.12%). NMR: 2.57 (s, 10 arom H); 3.63 (m, 4 vinylic H); 4.52 (m, 4 allylic H); 5.07 (dd, 1 H, C$\underline{H}$N); 5.90 (t, 2 H, $CO_2C\underline{H}_2$); 7.5–9.2 (m, 20 aliph H). Calculated NMR spectrum for vinylic H at 3.63 (A) and allylic H at 4.52 (B): $J_{AB} = J_{A'B'} = 5.3$ Hz; $J_{BB'} = 10$ Hz; $J_{A'B}$ $= J_{AB'} = 2.1$ Hz; $J_{AA'} = 0$. MS: 279 (20); 227 (100); 216 (12); 181 (27); 167 (21); 149 (40); 119 (54).

Photochemical cyclization of **9j** gave **10j** in 87% yield, m.p. 272° (CH_2Cl_2–hexane). (Found: N, 12.50; M.W. 747.3102. $C_{40}H_{41}N_7O_8$ requires: N, 13.12%; M.W. 747.3016). IR (KBr): 2900, 1780, 1740, 1500, 1400 cm^{-1}. NMR: 2.55 (s, 10 arom H); 4.95 (m, 4 bridgehead H); 5.10 (dd, 1 H, C$\underline{H}$N); 5.98 (t, 2 H, $CO_2C\underline{H}_2$, J = 6 Hz); 6.62 (m, 4 cyclobutane H). MS: M^+, 747 (100); 227 (56); 181 (34); 119 (24).

exo-*Bornyl 11′,13′dioxo-12′-aza[4.4.3]propella-3′,8′-diene-12′-(2S)-methylpentanoate* **7k**

To an ice-cooled soln of **7h** (3.17 g) in pyridine (100 ml) was added *p*-tosyl chloride (3.8 g) and after a few minutes *exo*-borneol (1.54 g, $[\alpha]_D = -24°$) and the whole was stirred for 3 days at room temp. The whole was poured into ice-water (500 ml) and extracted with C_6H_6. The extract was washed with NaCl aq–HCl aq to remove pyridine, dried and solvent removed, **7k** isolated after column chromatography on silica (80 g) using hexane–EtOAc (10:1) as eluant (4.38 g; 96%; $[\alpha]_D = -2.41°$), b.p. 160°/0.1 mm. (Found: N, 3.36.

$C_{28}H_{39}NO_4$ requires: N, 3.09%). IR: 2900, 1790, 1750, 1710, 1400 cm^{-1}. NMR: 4.0–4.3 (m, 4 vinylic H); 5.0–5.5 (m, 1 H, $C\underline{H}N$ + 1 H, $CO_2C\underline{H}$); 7.0–9.5 (m, 25 aliph H). MS: 317 (37); 300 (16); 272 (59); 204 (13); 151 (29); 137 (77); 136 (24); 121 (21); 81 (100).

exo-*Bornyl* 11′,13′-*dioxo*-12′-*aza*[4.4.3]*propella*-2′,4′,7′,9′-*tetraene*-12′-(2S)-4-*methylpentanoate*, **6k**

Prepared using benzene in 62% yield, b.p. 160°/0.1 mm. IR: 2900, 1790, 1740, 1720, 1400 cm^{-1}. NMR: 3.6–4.5 (A_2B_2, 8 vinylic H); 5.0–5.5 (m, 1 H, $C\underline{H}N$ + 1 H, $CO_2C\underline{H}$), 7.5–9.5 (m, 25 aliph H). MS: 268 (10); 220 (9); 205 (49); 137 (31); 128 (100).

Reaction of **6k** *with PTD*

(a) *At room temp.* Tetraene **6k** (343 mg in 10 ml) reacted immediately with PTD (95 mg; 0.72 eq in 5 ml). Removal of solvent gave recovered **6k** (65 mg), mono-adduct **11k** (157 mg; 41%) and mono-adduct **8k** (185 mg; 48%).

Mono-adduct **11k** had m.p. 142–143° (CH_2Cl_2–hexane). (Found: N, 8.85. $C_{36}H_{40}N_4O_6$ requires: N, 8.97%). IR (KBr): 2900, 1790, 1730 (br), 1400 cm^{-1}. NMR: 2.6 (s, 5 arom H); 3.4 (m, 4 vinylic H); 3.5–4.3 (A_2B_2, 4 dienic H); 4.8 (m, 2 allylic H); 5.0–5.5 (m, 1 H, $C\underline{H}N$ + 1 H, $CO_2C\underline{H}$); 7.7–9.5 (m, 25 aliph H). MS: 227 (43); 216 (26); 174 (19); 160 (89); 137 (98); 121 (35); 119 (96); 82 (100).

Mono-adduct **8k** had m.p. 189–190° (CH_2Cl_2–hexane). (Found: N, 9.10). IR (KBr): 2900, 1780, 1730 (br), 1400 cm^{-1}. NMR: 2.6 (s, 5 arom H); 3.4 (m, 2 vinylic H); 4.1 (m, 4 dienic H); 4.8 (m, 2 allylic H); 5.0–5.5 (m, 1 H, $C\underline{H}N$ + 1 H, $CO_2C\underline{H}$); 7.7–9.5 (m, 25 aliph H). MS: 227 (7); 131 (20); 119 (29); 69 (100).

Bis-adduct **12k** was prepared during a 2 min reaction between **11k** (48 mg in 5 ml) and PTD (14 mg in 3 ml). The product (60 mg; 98%) had m.p. 292° (dec, CH_2Cl_2–hexane). (Found: N, 11.54. $C_{44}H_{45}N_7O_8$ requires: N, 12.26%). IR (KBr): 2900, 1780, 1730 (br), 1500, 1400 cm^{-1}. NMR: 2.5 (s, 10 arom H); 3.3–3.6 (m, 4 vinylic H); 4.3–4.7 (m, 4 allylic H); 5.1–5.5 (m, 1 H, $C\underline{H}N$ + 1 H, $CO_2C\underline{H}$); 7.5–9.5 (m, 25 aliph H). MS: 331 (46); 227 (100); 183 (6); 160 (6); 133 (5); 121 (11), 119 (20).

Bis-adduct **9k** was prepared during 5 min reaction from **8k** (70 mg in 5 ml) and PTD (20 mg in 5 ml), giving product (85 mg; 95%), m.p. 287° (dec, CH_2Cl_2–hexane). (Found: C, 65.95; H, 5.69; N, 12.05; M.W. 799.3308. $C_{44}H_{45}N_7O_8$ requires: C, 66.07; H, 5.67; N, 12.26%; M.W. 799. 3337). IR (KBr): 2900, 1780, 1730 (br), 1500, 1400 cm^{-1}. NMR: 2.61 (s, 10 arom H); 3.72 (m, 4 vinylic H); 4.57 (m, 4 allylic H); 5.0–5.5 (m, 1 H, $C\underline{H}N$ + 1 H, $CO_2C\underline{H}$); 7.5–9.5 (m, 25 aliph H). MS: M^+, 799 (4); 227 (90); 169 (37); 142 (16); 136 (10); 121 (15); 119 (50).

(b) *At* −78°. **6k** (118 mg in 5 ml) with PTD (90 mg in 5 ml) gave during 1 hr **12k** (43 mg; 20%) and **9k** (80 mg; 38%).

Photochemical cyclization of **9k** gave **10k** in 83% yield, m.p. 300° (dec, CH_2Cl_2–hexane). (Found: N, 11.93). (IR (KBr): 2900, 1780, 1730 (br), 1400 cm^{-1}. NMR: 2.5 (s, 10 arom H); 4.9 (m, 4 bridgehead H); 6.6 (m, 4 cyclobutane H); 7.5–9.5 (m, 25 aliph H).

t-*Butyl* 11′,13′-*dioxo*-12′-*aza*[4.4.3]*propella*-3′,8′*diene*-12′-(2S)-4-*methylpentanoate*, **7l**

Compound **7h** (3.5 g), dry ether (10 ml), 2-methyl-propene (5 ml) and conc H_2SO_4 (3 drops) were shaken in a pressure bottle at room temp for 3 days until **7h** had completely dissolved. Solid Na_2CO_3 was added and the solvent removed, the residue taken up in C_6H_6 and filtered through a column of neutral alumina, C_6H_6 as eluant. Removal of benzene and distillation gave **7l** (2.0 g; 50%), b.p. 135/0,01 mm, m.p. 97–98° (CH_2Cl_2–hexane). (Found: N, 3.71. $C_{22}H_{31}NO_4$ requires N, 3.75%). IR (KBr): 2900, 1780, 1740, 1720, 1400 cm^{-1}. NMR: 4.0–4.3 (m, 4 vinylic H); 5.2 (dd, 1 H, $C\underline{H}N$, J = 16 Hz); 7.1–8.2 (m, 8 allylic H); 8.6 (s, 9 H, $-C(C\underline{H}_3)_3$); 8.1–9.3 (m, 9 aliph H). MS: 317 (36); 272 (56); 271 (38); 230 (33); 217 (30); 204 (34); 131 (27); 56 (100).

-*dioxo*-12′-*aza*[4.4.3]*propella*-2′,4′,7′,9-*tetraene*-12′-*t*-*Butyl* 11′13′-*dioxo*-12′-*aza*[4.4.3]*propella*-2′4′,7′9-*tetraene*-12′-(2S)-4-*methyl*-(2S)-4-*methylpentanoate*, **6l**

The tetraene was prepared using benzene in 70% yield, $[\alpha]_D = +0.18°$, m.p. 89–90° (pentane). IR (KBr): 2900, 1790, 1750, 1720, 1400 cm^{-1}. NMR: 3.8–4.6 (A_2B_2, 8 dienic H); 5.3 (dd, 1 H, $C\underline{H}N$, J = 16 Hz); 8.6 (s, 9 H, $C(C\underline{H}_3)_3$); 7.7–9.2 (m, 9 aliph H). MS: 296 (13); 268 (39); 205 (25); 128 (100).

Reaction of **6l** *with PTD*

(a) *At room temp.* **6l** (180 mg in 10 ml) was treated with excess PTD until red color persisted. Removal of solvent gave *bis*-adduct **12l** (160 mg; 53%) and bis-adduct **9l** (126 mg; 42%).

Bis-adduct **12l** had m.p. 185° (dec, CH_2Cl_2- hexane). (Found: N, 13.47. $C_{38}H_{36}N_7O_8$ requires: N, 13.62%). IR

Bis-adduct **12l** had m.p. 185° (dec, CH_2Cl_2–hexane). (Found: N, 13.47. $C_{38}H_{36}N_7O_8$ requires: N, 13.62%). IR
(KBr): 2950, 1790, 1730, 1500, 1400 cm^{-1}. NMR: 2.6 (s, 10 arom H); 3.2–3.5 (m, 4 vinylic H); 4.3–4.8 (m, 4 allylic H); 5.2–5.5 (m, 1 H, $C\underline{H}N$); 7.8–9.2 (m, 9 aliph H); 8.5 (s, 9 H, $C(C\underline{H}_3)_3$). MS: 193 (12); 227 (6); 133 (4); 119 (6).

Bis-adduct **9l** had m.p. 315° (dec, CH_2Cl_2-hexane). (Found: N, 13.50). IR (KBr): 2900, 1790, 1740, 1500, 1400 cm^{-1}. NMR: 2.64 (s, 10 arom H); 3.70 (m, 4 vinylic H); 4.64 (m, 4 allylic H); 5.83 (dd, 1 H, $C\underline{H}N$, J = 15 Hz); 7.8–9.2 (m, 9 aliph H) 8.6 (s, 9 H, $C(C\underline{H}_3)_3$). MS: 227 (100); 217 (17); 216 (68); 200 (11); 187 (15); 177 (26); 174 (74); 160 (100); 148 (29); 119 (100).

(b) At −78°: **6l** (117 mg in 15 ml) reacted with PTD (110 mg in 5 ml) during 5 min. Removal of solvent gave **12l** (66 mg; 34%) and **9l** (110 mg; 56%).

Photochemical cyclization of **9l** gave **10l** in 88% yield, m.p. > 320° (CH_2Cl_2-hexane). (Found: N, 13.54%). IR (KBr): 2850, 1790, 1750 (br) cm^{-1}. NMR: 2.5 (s, 10 arom H); 5.0 (m, 4 bridgehead H + 1 H, $C\underline{H}N$); 6.7 (m, 4 cyclobutane H); 7.8–9.2 (m, 9 aliph H); 8.6 (s, 9 H, $C(C\underline{H}_3)_3$). MS: 227 (100); 233 (5); 160 (6); 135 (5); 129 (7); 119 (37).

REFERENCES

[1] *Cf.* R. Gleiter and D. Ginsburg, *Pure Appl. Chem.* **51,** 1301 (1979).

[2] J. Kalo, E. Vogel and D. Ginsburg, *Tetrahedron* **33,** 117 (1977).

[3] J. Kalo and D. Ginsburg, *Ibid.* **34,** 2155 (1978).

[4] J. Kalo, J. J. Bloomfiled and D. Ginsburg, *Ibid.* **34,** 215 (1978).

[5] M. Korat, D. Tatarsky and D. Ginsburg, *Ibid.* **28,** 231 (1972).

[6] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.* **70,** 312 (1948).