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PROPELLANES—XXXVII

FURTHER TESTING OF THESIS REGARDING CONTROL BY SECONDARY ORBITAL OVERLAP DURING CERTAIN DIELS–ALDER REACTIONS†

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Abstract—We show again that compounds containing CO groups which are capable of secondary orbital interactions with the dienophile, 4-phenyl-1,2,4-triazoline-3,5-dione cause reaction to occur from above. However, in substrates which do not have capability for overlap with the dienophile nitrogen lone pairs and, on the contrary, exert steric hindrance to topside reaction, reaction with the first equivalent of dienophile occurs from below. When a second equivalent can react it reacts from above, again for relative steric reasons.

We have devoted much effort in testing the generality of the attack from above of propellanes containing CO groups by 4-phenyl-1,2,4-triazoline-3,5-dione (PTD). The transition state stabilized for reaction from above is shown schematically in Fig. 1.

Professor Rolf Gleiter has chosen the orbitals which are capable of efficacious overlap. These are the CO π^* orbitals (LUMO) with the unsymmetrical n combination of lone pair orbitals (HOMO) of the dienophile.[1] This is a secondary interaction since the important, primary, interaction is of course that involved between the p-orbitals of the diene and the p-orbitals of the N=N bond in the dienophile, leading to the thermal [4+2]cycloaddition involved in the Diels–Alder reaction.

We first invoked this idea to explain the exclusive attack of **1c** from above.[2] But this thesis was strengthened by the fact that three more methyl-imides related to **1c**, the diene and two possible trienes possessing the same skeleton, were attacked by PTD exclusively from above.[3] In this paper we report on two anhydrides and two imides which are also attacked by PTD exclusively from above. That **1a** and **1b** are attacked only from above is proved by formation of the *bis*-adducts **3a** and **3b**, respectively. Since the latter upon irradiation afford the cage compounds **4a** and **4b**, respectively, proving that *both* equivalents of dienophile attacked from above (this is the only way two double bonds can be in proximity for the ready [2+2]photocyclization), this means that the first equivalent of PTD also must have entered from above, proving the configurations of **2a** and **2b** respectively (Scheme 1). Since **2a** and **6a** both yield the same perhydro-compound on reduction, **5a** has also been attacked exclusively from the top side. The analogous configuration in the imide **6b** was correlated with its N–Me derivative of proven configuration.[3] Thus **5b** has also been attacked by PTD only from above. Incidentally, although this is merely additional evidence **3b** and **4b** have been correlated through N-methylation with the known **3c** and **4c**.[3]

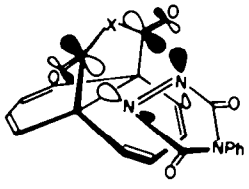


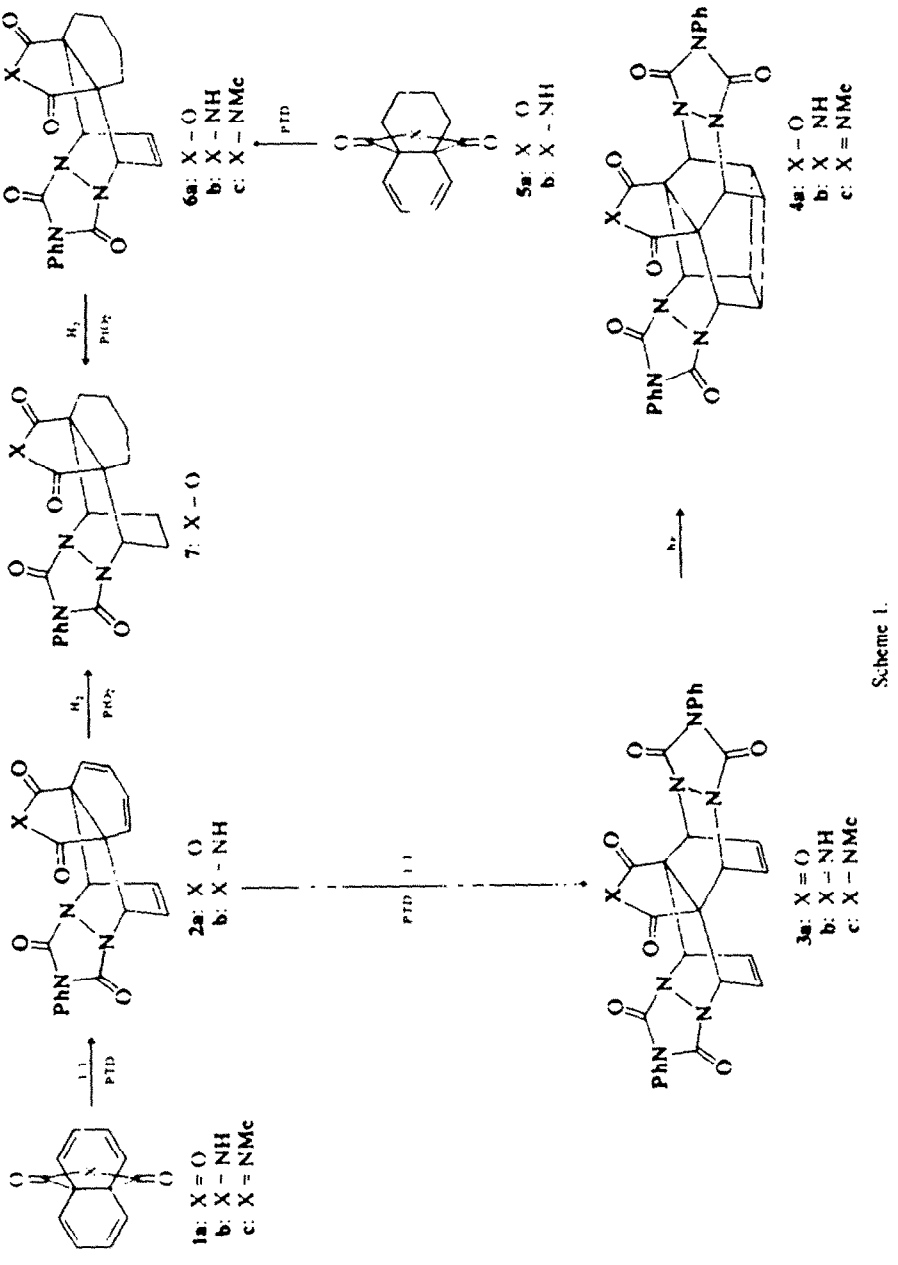
Fig. 1.

We have reported the behavior of the analogs *sans* carbonyls of **1a**, **5a** and a trienic member of the ether family. Since the CO oxygens are replaced by hydrogens which lack orbitals capable of effective overlap with the N-lone pair orbitals of PTD and since O-lone pairs of the ether are equally incapable, there is no help for attack from above. But, evidently the hydrogens moreover exert steric hindrance towards approach of PTD from above and attack occurs exclusively from below.[2,3] Similar behavior is exerted by cyclobutane hydrogens in the analogous [4.4.2]propellatetraene.[4] Again, [4.4.2]propellanes of different oxidation state are all attacked from below, even when a cyclobutene ring is present.[4] From the latter case we suspect that the orbitals that do not attract PTD, perhaps repel it. We have as yet insufficient evidence regarding this point.

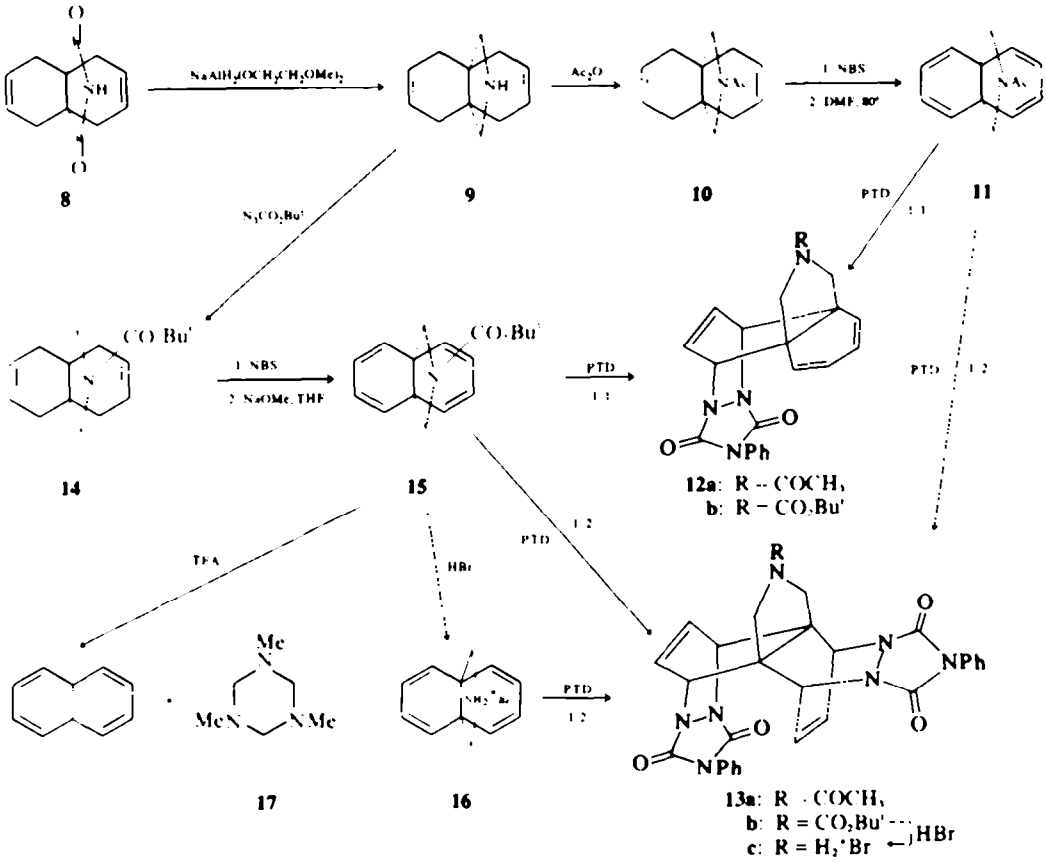
Clearly, one should prepare from imides such as **1b** the corresponding amine. The prediction would be that PTD should attack from below. That the second equivalent of PTD attacks from above is merely a tribute to the efficacy of PTD as a dienophile. Less energetic dienophiles react with the sterically hindering substrates only once, to afford the mono-adduct only.[2,4] This also means that the boat-shaped portion of the bicyclic moiety in the mono-adducts exerts more steric hindrance for attack by the second equivalent of PTD from below than do the hydrogens for attack from above.

The problem of reduction of a tetraenic propellane imide to a tetraenic propellane amine was a technical one. Reduction of the CO groups was accompanied by 1,4-reduction of the conjugated diene systems. Thus it was necessary to compromise on the approach, using blocking groups of the basic NH function, in order to

†Part XXXVI. P. Ashkenazi, E. Vogel and D. Ginsburg, *Tetrahedron* 33, 1169 (1977).



Scheme 1.



Scheme 2.

obtain derivatives of propellatetraenes containing an amino function (Scheme 2).

The amine **9** was treated alternatively with acetic anhydride and with t-butylazidoformate so that the NH group was blocked, affording **10** and **14**, respectively. Bromination followed by dehydrobromination could thus be effected and **11** and **15**, respectively, were obtained. These gave mono-adducts and *bis*-adducts, **12** and **13**, respectively, and the NMR spectra of **13a** and **13b** indicate that their structures are as shown. We have not proved unequivocally that **12a** and **12b** have the configuration shown; we choose this configuration in analogy to the behavior of the ethers discussed above in which we have proved unequivocally that the first equivalent of PTD attacks from below and the second from above, and not vice versa.[3] But we wanted to study the free tetraenic amine and removed the t-butyloxycarbonyl group from **15**. When this was done with TFA followed by the workup described in the Experimental we observed decomposition to yield naphthalene and the trimer **17** of the ammonium-ylide $CH_3\dot{N}-\bar{C}H_2 \leftrightarrow CH_3\bar{N}=CH_2$ which has already been described as the product when an attempt was made to prepare the monomer.[5]

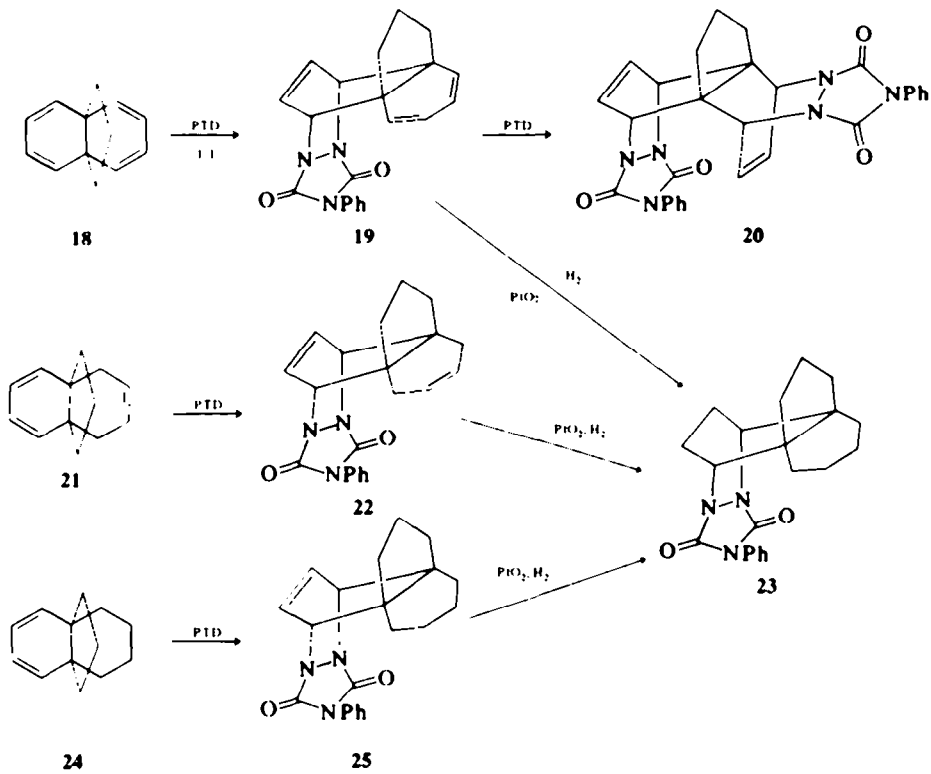
It is easy to explain the relative thermal stability[6] of the corresponding tetraene ether (O in place of NH). Ammonium ylides are more stable than oxonium-ylides.[7] This type of explanation does not carry over to the corresponding thioether (S in place of O or NH). We have studied the properties of the latter compound and it is thermally quite stable (up to 200°) despite the fact that a sulfonium-ylide should readily form along with naphthalene as a reasonable mode for the analogous decomposition. Perhaps the basicity of the amine is the paramount cause of its instability.

When **15** was treated with HBr the hydrobromide salt of the tetraenic amine was readily isolated. Its basification gave the free amine which rapidly gave naphthalene and **17**. But the salt **16** afforded with PTD the salt **13c** which could alternatively be prepared by treatment of the *bis*-adduct **13b** with HBr. Thus, the amine salt **16** is also attacked by PTD as are **11** and **15**.

Finally we studied a series of [4.4.3]propellanes containing one or two conjugated dienes (Scheme 3). Here steric hindrance from above is greater than in the ethers,[3] and the [4.4.2]propellane substrates reported earlier.[4] They should be more comparable to the compounds described in Scheme 2. The reaction course for **18**, **21** and **24** is identical. Although we have not shown this unequivocally by chemical means, we proved by the latter means that the mono-adducts **19**, **22** and **25** all possess identical configuration since they all give the same perhydro-derivative **23**, upon reduction. But X-ray structural determination of **25** shows that it indeed has the configuration shown in Scheme 3.[8] That **20** is of C_s rather than C_2, symmetry is clearly indicated by its NMR spectrum. The X-ray work proves that **20** is formed by the chronology predicted: the first equivalent of PTD attacks from below, the second from above.

EXPERIMENTAL

IR spectra were measured (in $CHCl_3$ unless otherwise specified) using a Perkin Elmer 257 or 237 spectrometer. NMR spectra were measured on Varian T-60 or A-60 instruments (given in τ values)



Scheme 3.

and mass spectra on an Atlas CH4 (70 eV) or a Varian MAT-711 (100 eV) mass spectrometer. M.ps are uncorrected. Organic solutions dried over anhyd $MgSO_4$. Solvents were removed in a rotary evaporator at water pump pressure. Preparative silica plates were 20 × 20 cm of 70 g silica gel 60 PF 254 produced by E. Merck. Degassing of solutions before irradiation was carried out by a series of 4 freezing and melting operations at 10^{-3} torr.

General procedure for Diels–Alder reactions. A soln of the substrate in CH_2Cl_2 was treated with one of 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) in CH_2Cl_2 at room temp. whilst stirring magnetically. When the red color had disappeared the solvent was removed and the crude products, usually obtained in practically quantitative yield were recrystallized. If another solvent was used this is specified.

Mono-adduct **2a**

Anhydride **1a**[9] (100 mg) in 4 ml gave with dienophile (PTD) (88 mg) in 3 ml instantaneously, **2a**. After trituration with benzene it had m.p. 222–224° (dec). (Found: 227.0667 M^+-$C_6H_4O_2$ (retro-D.A.) requires: 227.0694). IR 2940, 1785, 1725, 1405 cm^{-1}. NMR (DMSO-d_6): 2.53 (s, 5 arom H); 3.37 (t, 2 vinylic H, J = 3 Hz); 3.80–4.23 (m, 4 dienic H); 4.43 (t, 2 CHN, J-3 Hz). MS. 228(11), 227(100), 119(40).

Bis-adduct **3a**

Compound **2** (75 mg) in 12 ml with PTD (35 mg) in 5 ml discharged the red color after 1 hr. **3a** had m.p. 297–298° (dec, CH_2Cl_2). (Found: C, 60.92; H, 3.17; N, 15.30. $C_{28}H_{18}N_4O_4$ requires: C, 61.09; H, 3.30; N, 15.27%). IR (KBr): 3060, 3020, 1870, 1780, 1710, 1590, 1490, 1400 cm^{-1}. NMR (DMSO-d_6): 2.57 (s, 10 arom H); 3.60 (t, 4 vinylic H, J = 3 Hz); 4.36 (t, 4 CHN, J = 3 Hz). MS. 228(14), 227(96), 128(11), 120(13), 119(100).

Irradiation of **3a**

A soln of **3a** (70 mg) in acetone (70 ml) was degassed and irradiated in a Rayonet reactor at 300 nm during 72 hr. After evaporation of solvent and trituration with CH_2Cl_2 the pure cage compound **4a**, had m.p. >350°. (Found: C, 59.49; H, 3.48; N, 14.83. $C_{28}H_{18}N_4O_4$ requires: C, 61.09; H, 3.30; N, 15.27%). IR (KBr): 3000, 1845, 1825, 1760, 1550, 1475, 1400 cm^{-1}. NMR (DMSO-d_6): 2.50 (s, 10 arom H); 5.00 (br s, 4 CHN); 6.77 (br s, 4 cyclobutane H). MS. 549(36), 228(42), 227(100), 119(63), 109(18).

Mono-adduct **6a**

Anhydride **5a**[10] (102 mg) in 3 ml with PTD (88 mg) in 5 ml gave instantaneously **6a**, m.p. 276–277° (acetone). (Found: M.W. 379.1187. $C_{20}H_{13}N_3O_4$ requires: 379.1196). IR: 2950, 1785, 1725, 1410 cm^{-1}. NMR (DMSO-d_6): 2.57 (s, 5 arom H); 3.30 (t, 2 vinylic, J = 3 Hz); 4.78 (t, 2 CHN, J = 3 Hz); 7.67–9.00 (m, 8CH_2). MS. M^+ 379(7), 228(14), 227(100), 119(26), 104(7).

Reduction procedure

A soln of **2** (70 mg) in AcOH (60 ml) was reduced using PtO_2 (5 mg) at atm. pressure during 24 hr. Removal of catalyst and solvent gave the pure product **7** after trituration with MeOH, m.p. 293–294°. (Found: N, 10.67. $C_{20}H_{14}N_2O_4$ requires: N, 11.02%). IR (KBr): 2940, 2860, 1850, 1780, 1700 cm^{-1}. MS. 227(100), 128(10), 119(40), 105(30).

Reduction of **6a** analogously gave **7**, m.p. and m.m.p. 292–293° with IR spectrum identical to the above sample.

The mono-adduct **2b** has been prepared earlier.[2]

Bis-adduct **3b**

The color of the mixture of **1b** (100 mg) in 5 ml with PTD (175 mg) in 5 ml was discharged after 30 min. The product **3b** had m.p. 282–284° (dec, acetone). (Found: M^+-$C_{12}H_8N_2O_2$: 322.0702, requires: 322.0732; Found: M^+-$C_{16}H_{10}N_4O_4$: 227.0693, requires: 227.0695). IR (KBr): 3240, 1780, 1720, 1500, 1405 cm^{-1}. NMR (DMSO-d_6): 2.50 (s, 10 arom H); 3.67 (t, 4 vinylic H, J = 3 Hz); 4.50 (t, 4 CHN, J = 3 Hz). MS. 322(7), 228(5), 227(26), 180(67), 171(7), 170(6), 147(59), 141(6), 120(10), 119(100).

Methylation of **3b** with ethereal CH_2N_2 gave the N-Me derivative, m.p. 277–278°, identical by m.m.p. and spectroscopically with authentic specimen, m.p. 277–278°.[2]

Irradiation of **3b**

Analogously to that of **3a** above, gave the cage compound **4b**, m.p. >360°. (Found: M.W. 549.1402. $C_{28}H_{18}N_4O_4$ requires:

549.1342). IR (KBr): 2970, 2780, 1730, 1700, 1500 cm $^{-1}$. NMR (DMSO-d_6 + TFA): 2.50 (s, 10 arom H); 4.50, 4.73 (m, 4 CHN); 6.60–6.77 (m, 4 cyclobutane H). MS. M$^+$ 549(16), 367(9), 231(100), 163(17), 151(28), 133(13), 119(59).

Methylation gave as above the N-Me derivative, m.p. >350°, identical with the corresponding authentic sample spectroscopically.[2]

Mono-adduct **6b**

The imide **5b** (51 mg) in 4 ml and PTD (41 mg) in 4 ml reacted at once. The adduct **6b** had m.p. 349–351° (dec) after trituration with MeOH. (Found: M.W. 378.1297. $C_{20}H_{18}N_4O_4$ requires: 378.1266). IR (KBr): 3160, 3060, 2940, 1770, 1715, 1490, 1410 cm $^{-1}$. NMR (DMSO-d_6): 2.50 (s, 5 arom H); 3.30 (t, 2 vinylic H, J = 3 Hz); 5.00 (t, 2 CHN, J = 3 Hz); 7.90–9.00 (m, 8 CH_2). MS. M$^+$ 378(10), 228(12), 227(100), 119(23), 104(8).

Methylation as above gave the N-Me derivative, m.p. 258–260° identical with the authentic sample m.p. 262–263° by m.m.p. 259–261° and spectroscopically.[3]

12-*Aza*[4.4.3]*propella*-3,8-*diene*, **9**

To a cold soln of **8**[3] (2.4 g) in benzene (75 ml) was added dropwise $NaAlH_2(OCH_2CH_2OCH_3)_2$ (70% in C_6H_6; 15 ml) and then the whole was heated under reflux (N_2) during 48 hr. Excess reagent was decomposed after cooling by addition of KOH (30% aq) and the organic phase was dried. After removal of solvent, **9** was obtained as an oil (1.7 g; 80%), b.p. 85° (0.1 mm). MS. 175(35), 174(42), 129(22), 130(10), 105(100). The amine gave a hydrate, m.p. 125–128°. The *picrate* formed in methanol had m.p. 209–210° (methanol). (Found: C, 53.61; H, 5.02; N, 13.63. $C_{18}H_{20}N_4O_7$ requires: C, 53.46; H, 4.99; N, 13.86%). **9**: IR: 3350, 2880, 1650, 1440, 1420 cm $^{-1}$. NMR ($CDCl_3$): 4.37–4.50 (m, 4 vinylic H); 7.10 (s, 4 CH_2N); 7.56 (s, NH); 8.00 (br s, 8 allylic H). NMR of hydrate ($CDCl_3$): 4.34–4.67 (m, 4 vinylic H); 6.70, 6.90 (2 br s, 4 CH_2N); 8.00 (br s, 8 allylic H).

Acetylation of **9**

A soln of **9** (160 mg) in Ac_2O (3 ml) was heated under reflux during 1 hr. After removal of solvent the acetamide **10** (170 mg; 85%) had b.p. 120° (0.1 mm), m.p. 54–56°. (Found: C, 76.95; H, 8.76; N, 6.29; M.W. 217.1448. $C_{14}H_{19}NO$ requires: C, 77.38; H, 8.81; N, 6.45%; M.W. 217.1465). IR: 2980, 2880, 1630, 1440 cm $^{-1}$. NMR (CCl_4): 4.56 (br s, 4 vinylic H); 6.70 (s, 4 CH_2N); 7.95 (s, 8 allylic H); 8.10 (s, 3 $COCH_3$). MS. M$^+$ 217(100), 174(26), 162(22), 160(10), 143(16), 129(26), 120(51), 118(12).

Preparation of **11**

To a soln of **10** (1.1 g) in CCl_4 (50 ml) was added freshly crystallized NBS (2.0 g) and a trace of dibenzoyl peroxide. The reaction was over after a reflux period of 20 min. After the usual workup the crude bromide was taken up in the dry DMF (20 ml) and the solution was maintained at 80° under N_2 overnight. After the usual workup the crude product was purified by chromatography on a column of basic alumina (grade I; 20 g) using chloroform (1):hexane (4). An oil was obtained (45%) but was unstable and should be used at once. (Found: M.W. 213.1148. $C_{14}H_{15}NO$ requires: 213.1153). IR: 3000, 1640, 1450, 1420 cm $^{-1}$. NMR ($CDCl_3$): 3.90–4.67 (AA'BB', 8 dienic H); 6.15, 6.45 (ABq, 4 CH_2N, J = 12 Hz); 8.00 (s, 3 $COCH_3$). MS. M$^+$ 213(6), 205(24), 141(88), 129(100).

Mono-adduct **12a**

Immediate reaction occurs between **11** (22 mg) in 2 ml and PTD (18 mg) in 2 ml, affording **12a**, m.p. 197–199° (EtOH). (Found: N, 14.38. $C_{22}H_{20}N_4O_4$ requires: N, 14.43%). IR: 2980, 1770, 1715, 1640, 1500, 1410 cm $^{-1}$. NMR ($CDCl_3$): 2.53 (s, 5 arom H); 3.30 (t, 2 vinylic H, J = 3 Hz); 3.67–4.34 (m, 4 dienic H); 5.13 (t, 2 CHN, J = 3 Hz); 6.22, 6.44 (ABq, 4 CH_2N, J = 13 Hz); 8.00 (s, 3 $COCH_3$). MS. 227(21), 215(21), 161(18), 141(21), 129(66), 128(100).

Bis-adduct, **13a**

Immediate reaction occurs also between **11** (110 mg) in 2 ml and 2 eq PTD (175 mg) in 4 ml, yielding **13a**, m.p. 240–242° (EtOH–ether). (Found: N, 17.40. $C_{36}H_{32}N_8O_8$ requires: N, 17.42%). IR: 2920, 1770, 1720, 1650, 1500, 1410 cm $^{-1}$. NMR ($CDCl_3$): 2.50 (s, 10 arom H); 3.34 (t, 2 vinylic H, J = 3 Hz); 3.50 (t, 2 vinylic H, J = 3 Hz); 4.80–5.10 (m, 4 CHN); 5.93, 6.47 (ABq, 4 CH_2N, J = 12 Hz); 8.00 (s, 3 $COCH_3$). MS. 227(35), 161(100), 144(25).

Preparation of **14**

To a soln of **9** (350 mg) in THF (5 ml) was added aq (1 ml) NaOH (400 mg) and t-butylazidoformate (350 mg). Stirring was maintained overnight at room temp, the organic phase separated and the solvent removed. The crude residue had b.p. 130° (0.1 mm), solidified after distillation (420 mg; 76%), m.p. 78–80°. (Found: C, 73.39; H, 8.82; N, 5.35; M.W. 275.1894. $C_{16}H_{25}NO_2$ requires: C, 74.14; H, 9.15; N, 5.09%; M.W. 275.1885). IR: 2980, 2900, 1670, 1630, 1460 cm $^{-1}$. NMR ($CDCl_3$): 4.34–4.50 (m, vinylic H); 6.83 (d, 4 CH_2N, J = 4 Hz); 8.00 (s, 8 allylic H); 8.50 (s, 9C(CH_3)$_3$). MS. M$^+$ 275(14), 219(100), 217(98), 205(58), 174(77), 162(28), 158(33), 145(60), 130(26), 121(22), 120(70), 116(15), 104(16).

Preparation of **15**

As for **11** using **14** (1.1 g), NBS (1.7 g), CCl_4 (30 ml) and catalyst. The crude bromide analogously obtained was dissolved in dry THF (30 ml) and NaOMe (3.0 g) was added. After heating under reflux (N_2) overnight and the usual workup the crude product was distilled, b.p. 135° (0.1 mm), affording solid **15** (450 mg; 40%), m.p. 67–69°. It is not stable for long periods. IR: 2980, 1680, 1410 cm $^{-1}$. NMR ($CDCl_3$): 4.00–4.67 (m, 8 dienic H); 6.37 (br s, 4 CH_2N); 8.53 (s, 9C(CH_3)$_3$). MS. 232(5), 205(24), 128(100).

Mono-adduct **12b**

Immediate reaction occurred between **15** (27 mg) in 2 ml and PTD (18 mg) in 2 ml, affording crude product, purified on a silica plate using acetone (1):hexane (3). Pure **12b** had m.p. 207–209° (dec). (Found: C, 67.75; H, 6.98. $C_{24}H_{26}N_4O_4$ requires: C, 67.25; H, 5.87%). IR: 2930, 1760, 1710, 1400 cm $^{-1}$. NMR ($CDCl_3$): 2.57 (s, 5 arom H); 3.34 (t, 2 vinylic H, J = 3 Hz); 3.67–4.34 (m, 4 dienic H); 5.17 (t, 2 CHN, J = 3 Hz); 6.26, 6.73 (ABq, 4 CH_2N, J = 12 Hz); 8.57 (s, 9C(CH_3)$_3$). MS. 227(100), 162(25), 149(41), 139(26), 125(40), 123(34).

Bis-adduct **13b**

Immediate reaction occurred also between **15** (27 mg) in 2 ml and 2 eq PTD (35 mg) in 2 ml, affording **13b**, m.p. 234–236° (dec, acetone-*i*-propyl ether). (Found: N, 15.72. $C_{34}H_{34}N_8O_8$ requires: N, 15.82%). IR: 3000, 1770, 1720, 1500, 1400 cm $^{-1}$. NMR ($CDCl_3$): 2.50 (s, 10 arom H); 3.34 (t, 2 vinylic H, J = 3 Hz); 3.53 (t, 2 vinylic H, J = 3 Hz); 4.83–5.13 (m, 4 CHN); 6.00, 6.50 (ABq, 4 CH_2N, J = 12 Hz); 8.53 (s, 9C(CH_3)$_3$). MS. 227(85), 177(30), 119(100).

Treatment of **15** *with acid*

(a) A soln of **15** (120 mg) in trifluoroacetic acid (4 ml) was stirred at room temp. overnight. The acid was removed at the water pump and the oily residue dissolved in $CHCl_3$ and washed with 1 M $NaHCO_3$. After drying and removal of solvent the residue was distilled at 80° (0.1 mm). Two fractions were collected at −78° (40 mg) and at −180° (10 mg). Purification of the first on a column of basic alumina (grade I; 3 g) using hexane afforded pure naphthalene, identical with an authentic sample. The second fraction gave the trimer **17**, an oil identical with an authentic sample prepared by the literature procedure.[3]

(b) A soln of **15** (50 mg) in dry ether (10 ml) was treated with HBr gas during 8 min. The ppt of oily **16**, which solidified was stable and could be used to undergo reaction with PTD.

Preparation of **13c**

(a) HBr gas was bubbled into a soln of **13b** (120 mg) in dry ether (10 ml) during 8 min. The precipitated salt, **13c** had m.p. 229–231° (dec). (Found: 227.0701. M.W.-$C_{16}H_{14}N_4O_2$ (retro-D.A.)-HBr requires: 227.0694). 1700, 1450 cm $^{-1}$. MS. 227(10), 196(10), 175(48), 157(20), 145(48), 119(100).

(b) A soln of **16** (50 mg) in acetone (2 ml) was treated with PTD (60 mg) in acetone (2 ml) affording after 30 min reaction and removal of solvent crude salt which was triturated with MeOH–ether; m.p. 227–229° (dec), identical with **13c** described above by mixed m.p. 228–230° (dec) and spectroscopically.

Mono-adduct **19**

An instantaneous reaction occurred between **18**, kindly prepared by Mr. Bobisch of the University of Köln (34 mg) in 3 ml and PTD (35 mg) in 3 ml, affording **19**, m.p. 194–195° (benzene–hexane). (Found: C, 73.26; H, 5.91; N, 11.82. $C_{21}H_{19}N_3O_2$ requires: C, 73.02; H, 5.55; N, 12.17%). IR: 2940, 2850, 1780, 1725, 1615, 1510, 1415 cm^{-1}. NMR ($CDCl_3$): 2.57 (s, 5 arom H); 3.40 (t, 2 vinylic H, J = 3 Hz); 3.90–4.50 (AA'BB', 4 dienic H); 5.23 (t, 2 CHN, J = 3 Hz); 8.00–8.67 (m, 6 CH_2). MS. 279(19), 227(25), 167(37), 150(13), 149(100), 133(23), 119(22), 117(20), 113(10).

Bis-adduct **20**

Immediate reaction also occurred between **19** (138 mg) in 4 ml and PTD (70 mg) in 4 ml giving **20**, m.p. 280–282° (dec, benzene–hexane). (Found: C, 67.12; H, 4.69; N, 15.89; M.W. 520.1848. $C_{30}H_{24}N_8O_4$ requires: C, 66.91; H, 4.65; N, 16.15%; M.W. 520.1858). IR: 1785, 1730, 1615, 1510, 1410 cm^{-1}. NMR ($CDCl_3$): 2.50 (s, 10 arom H); 3.43 (t, 2 vinylic H, J = 3 Hz); 3.60 (t, 2 vinylic H, J = 3 Hz); 4.95–5.16 (m, 4 CHN); 7.50–8.67 (m, 6 CH_2). MS. M$^+$ 520(24), 227(54), 181(100), 149(9), 119(18).

Mono-adduct **22**

Immediate reaction occurred between **21**, kindly prepared by Mr. Bobisch of Köln (35 mg) and 3 ml and PTD (35 mg) in 2 ml, giving **22**, m.p. 180–182° (benzene–hexane) after purification on a column of basic alumina (grade I; 3 g) using chloroform (1):hexane (9). (Found: C, 71.54; H, 5.93; N, 11.80. $C_{21}H_{21}N_3O_2$ requires: C, 71.60; H, 6.09; N, 12.10%). IR: 2940, 2920, 1785, 1725, 1620, 1515, 1415 cm^{-1}. NMR ($CDCl_3$): 2.50 (s, 5 arom H); 3.40 (t, 2 vinylic H, J = 3 Hz); 3.83–4.07 (m, 2 vinylic H); 5.40 (t, 2 CHN, J = 3 Hz); 7.34–8.80 (m, 10 CH_2). MS. 227(12), 165(21), 120(19), 119(100), 102(96).

Mono-adduct **25**

Immediate reaction occurred between **24**, kindly prepared by Mr. Bobisch of Köln (58 mg) in 2 ml and PTD (58 mg) in 3 ml, affording **25**, m.p. 198–199° (benzene–hexane). (Found: C, 71.99; H, 6.49; N, 12.02; M.W. 349.1755. $C_{21}H_{23}N_3O_2$ requires: C, 72.18; H, 6.63; N, 12.03%; M.W. 349.1790). IR: 2940, 2860, 1750, 1695, 1400 cm^{-1}. NMR ($CDCl_3$): 2.53 (s, 5 arom H); 3.50 (t, 2 vinylic H, J = 3 Hz); 5.47 (t, 2 CHN, J = 3 Hz); 7.50–8.80 (m, 14 CH_2). MS. M$^+$ 349(9), 227(100), 119(24).

Reduction procedure

(a) A soln of **19** (50 mg) in EtOAc (70 ml) was reduced at 40 psi using PtO_2 (8 mg) during 1 hr. Removal of catalyst by filtration through cellulose and removal of solvent gave the perhydro-derivative **23**, quantitatively, m.p. 197–198° (benzene–ether). (Found: C, 71.69; H, 7.17; N, 12.04; M.W. 351.1935. $C_{21}H_{25}N_3O_2$ requires: C, 71.77; H, 7.17; N, 11.96%; M.W. 351.1946). IR: 2920, 1775, 1710, 1615, 1515 cm^{-1}. NMR ($CDCl_3$): 2.20–2.63 (m, 5 arom H); 6.00 (br s, 2 CHN); 7.67–8.64 (m, 18 CH_2). MS. M$^+$, 351(100), 228(59), 227(7), 174(90).

(b) Analogous reduction of **22** afforded **23**, m.p. 194–196°, m.m.p. with above sample 195–197° and identical spectroscopically.

(c) Analogous reduction of **25** afforded **23**, m.p. 194–195°, m.m.p. with authentic sample, 195–196° and identical spectroscopically.

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REFERENCES

[1]R. Gleiter, private communications.
[2]M. Korat, D. Tatarsky and D. Ginsburg, *Tetrahedron* **28**, 2315 (1972).
[3]C. Amith and D. Ginsburg, *Ibid.* **30**, 3415 (1974).
[4]J. Kalo, J. M. Photis, L. A. Paquette, E. Vogel and D. Ginsburg, *Ibid.* **32**, 1013 (1976).
[5]E. M. Smolin and L. Rapoport, *The Chemistry of Heterocyclic Compounds, s-Triazines and Derivatives* (Edited by A. Weissberger), p. 477. Interscience, New York (1959).
[6]J. Altman and D. Ginsburg, *Tetrahedron* **27**, 93 (1971).
[7]V. Markowski, Ph.D. Dissertation, Univ. München, private communication from Professor R. Huisgen, 5 Nov. 1974.
[8]M. Kaftori, Private communication.
[9]W. Meckel, Ph.D. Dissertation, Univ. Köln (1965). *Cf.* L. A. Paquette and M. J. Carmody, *J. Am. Chem. Soc.* **97**, 5847 (1975).
[10]C. Amith, J. Kalo, B. E. North and D. Ginsburg, *Tetrahedron* **30**, 479 (1974).
[11]N. Bobisch, Staatsexamensarbeit, Universität Köln (1976).