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PROPELLANES—XLII

SECONDARY-ORBITAL-OVERLAP CONTROL DURING CERTAIN DIELS–ALDER REACTIONS†

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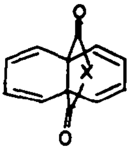
Abstract—We show additional cases of Diels–Alder reactions between propellane imides. When bulky substituents are attached to the imide-nitrogen, their steric effect partly offsets the electronic influence of the CO groups in overlapping with the dienophile nitrogen lone pairs.

We have explained the exclusive direction of attack, from *above*, of propellanes containing two CO groups through stabilization of the transition state in a Diels–Alder reaction between the diene (type 1) COπ^* orbitals (LUMO) with the unsymmetrical *n* combinations of lone pair orbitals (HOMO) of a 4-substituted-1,2,4-triazoline-3,5-dione dienophile.[1]

When H atoms hinder the approach of the dienophile from above (type 2 substrates), attack occurs exclusively from below.[1] When H atoms, Me groups, or lone pairs hinder attack from above, owing to the relative proximity of the bridge to the plane of the annulene molecule (type 3), then even a second equivalent of dienophile attacks from below. In the previous cases (1 and 2) the second equivalent of dienophile attacks from *above*, for steric reasons, i.e. the boat conformation exerting steric hindrance towards attack from below by the second equivalent of dienophile overcomes that exerted by the hydrogens towards attack from above in compounds of type 2. For compounds of type 1 there are no such hydrogens (their place is taken by CO groups) so that the second equivalent of dienophile certainly prefers to attack from above for both steric *and* electronic reasons (Scheme 1).



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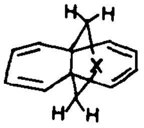

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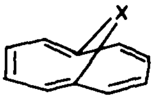

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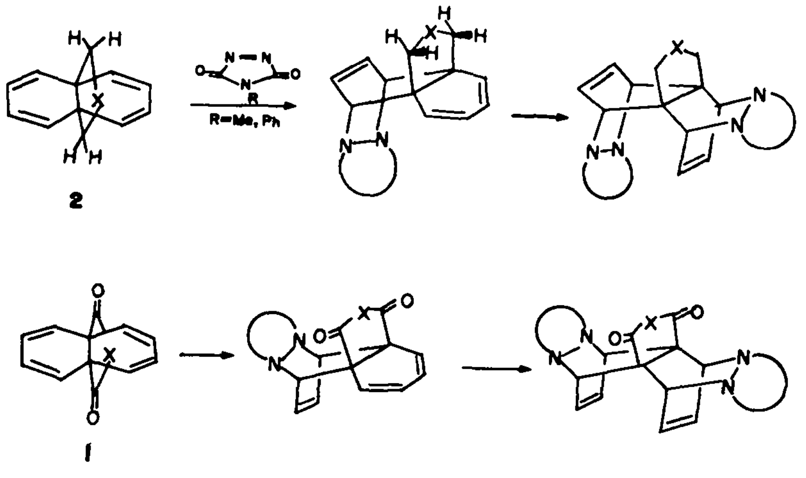

Scheme 1.

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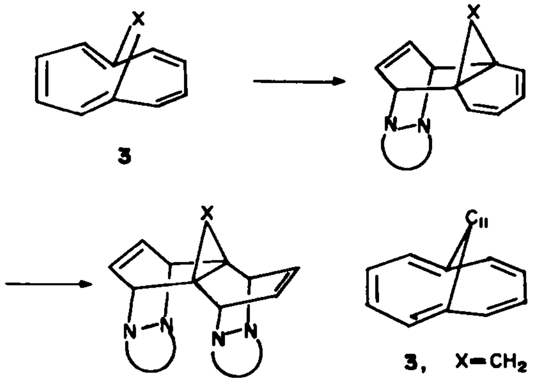
†Part XLI: J. Kalo, J. J. Bloomfield and D. Ginsburg, *Tetrahedron* **34**, 2153 (1978).

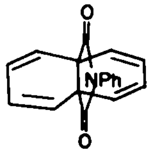
For bridged[10] annulenes, as stated above, we have again a *bis*-adduct of C_{2v} symmetry as for type 1 but the configuration is reversed (Scheme 2).[2]



Scheme 2.

What else may be envisaged in order to support (or defeat) our thesis regarding secondary orbital control of the direction chosen by the dienophile to attack the diene? One may introduce polar groups into type 3 substrates as substituents in the 11-positions of 1,6-methano[10] annulene, 3; $X = CH_2$, in the hope, slight though this be, (for the geometry does not make for efficacious overlap as in the case of type 1 substrates), that attack will be reversed at least in part and some attack will indeed occur from above. This is being done and the compounds supplied intermittently from Köln are subjected in Haifa to attack by the dienophile; the first results are being described concurrently.[3]

Alternatively (and concurrently) one may introduce bulky groups into type 1 compounds in the hope that if our thesis is correct then our prediction that we would interfere with the efficacious overlap with the same dienophiles, and thus get attack also from below, would also be correct. We describe herein our results concerning Diels–Alder reactions of three substrates of type 1, 4, 5 and 6 respectively. The three substituents on the imide nitrogen are, *prima facia*, all bulky but our results show that only those in 5 and in 6 can be classified as such. The phenyl group in 4 does not behave differently than any of the compounds, listed above, of type 1.



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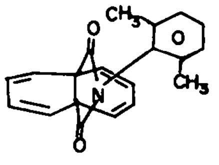

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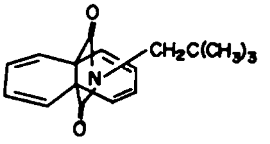

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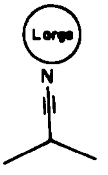
We should very much have wanted similar derivatives at the amine oxidation level, i.e. type 2, X = NPh, N-(2, 6-Dimethylphenyl), $NCH_2C(Me)_3$. Had the lattter substrates been available we might obtain attack by *both* equivalents of dienophile from below because of the large steric hindrance towards attack from above. However, we have already discussed the difficulties in preparing such amines and their relative instability.[1] We therefore had to make do with the substrates 4–6 of type 1 in which the Newman projection is 7 rather than 8, that for the amine oxidation state. Thus, *a priori*, the steric "umbrella" protecting both top faces of 7 towards a dienophilic rain, is in principle less effective than that obtaining in 8, were the latter umbrella available. We still have designs regarding the obtention of the more effective propellane—*parapluie*. But so long as bread is unavailable cake must suffice.[4]



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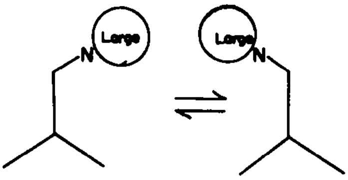

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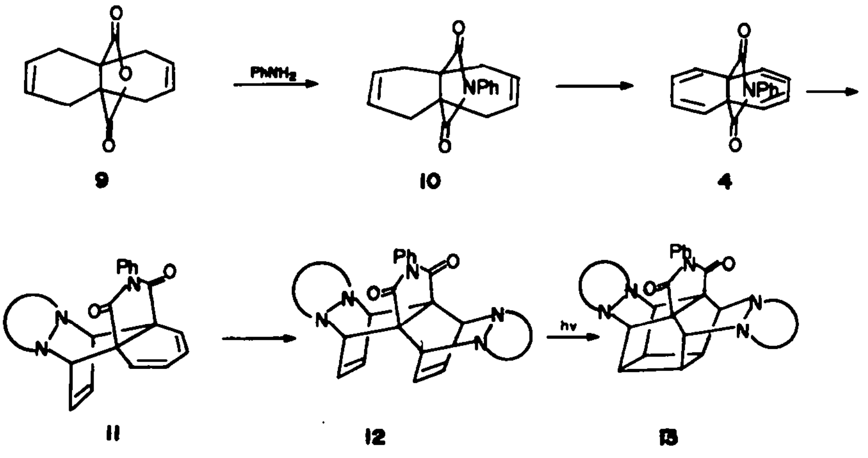
The tetraenic N-phenylimide 4 was prepared as shown in Scheme 3. The dienic anhydride 9 upon reaction with



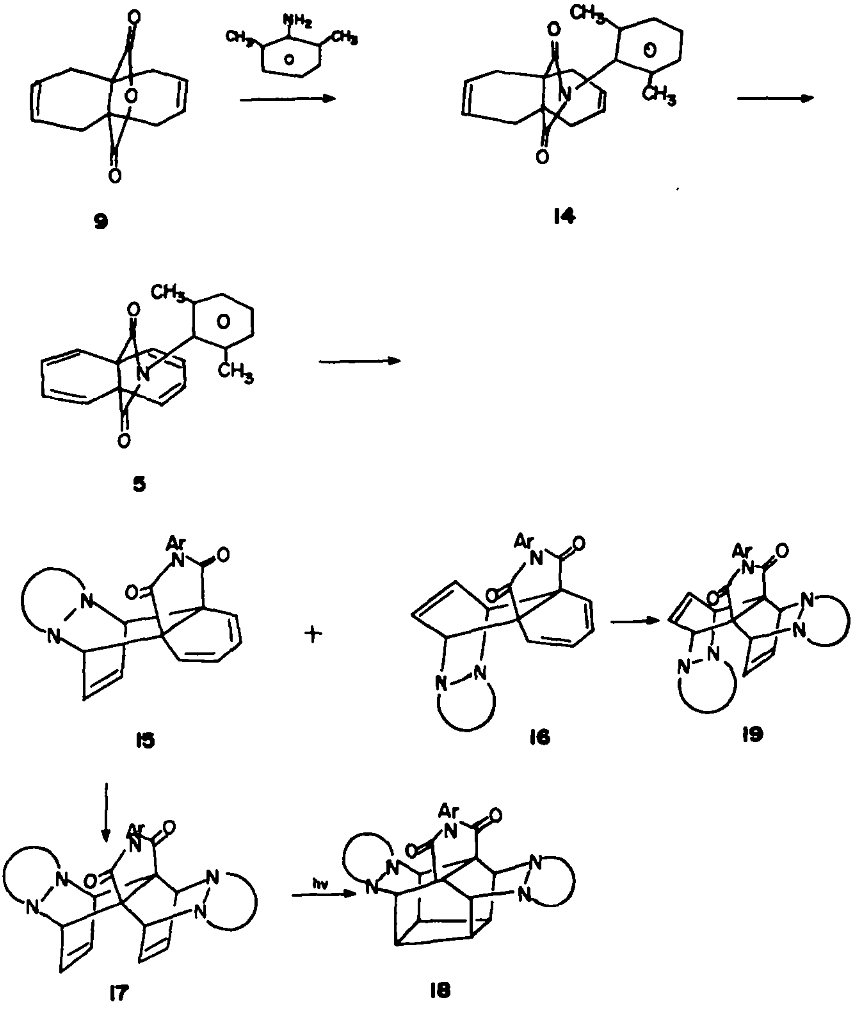
Scheme 3.

aniline at 75° afforded the dienic phenylimide **10**. Bromination followed by dehydrobromination gave **4**.

Reaction of **4** with the first equivalent of 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) afforded only one mono-adduct, **11**, in quantitative yield. That **11** had the configuration shown is obvious; for **11** quantitatively yields the *bis*-adduct, **12**, of C_{2v} symmetry, which in turn, upon irradiation affords the [2 + 2] photocyclization product **13**.†

The dienic 2,6-dimethylphenylimide **14** was obtained analogously by heating the anhydride **9** with 2,6-dimethylaniline at 110°. This was converted into the tetraenic analog **5** by bromination-dehydrobromination as above. Scheme 4 shows, in contradistinction to the unsubstituted phenylimide that indeed two mono-adducts **15** and **16** were obtained, the former leading to the *bis*-adduct **17**, of C_{2v} symmetry and of the configuration shown as shining light upon **17** afforded **18** again as a result of a [2 + 2]photocycloaddition. On the other hand, the isomeric mono-adduct **16** led to the bis-adduct **19** of C_s symmetry. Thus we see that the two Me groups ortho to the point of attachment of the aromatic nucleus to the imide-N atom exert sufficient steric hindrance so that **16** is formed in addition to **15**. When these Me groups are, instead, H atoms, only **11** is obtained by attack exclusively from above. This does not necessarily mean that complete free rotation may occur about the N-Ph bond in **9**. Perhaps a specific conformation is preferred so that 2,6-hydrogens cannot be effective in exerting sufficient steric hindrance on top side so as to affect the product distribution. Alternatively, perhaps free rotation about the N-Ph bond is possible but the 2,6-hydrogens are too far from the entry-site of the dienophile to affect the latter one way or the other.

Clearly when we have 2,6-Me groups there is either a specific preferred conformation with respect to the N-aryl bond, or in any event, there must be restricted rotation in such a way that the Me groups do interfere with the entry site of the dienophile from above, sufficiently to cause some reaction to occur from below. We have observed the PMR spectra of **5** as well as those of its adduct at low temperature as well as at room temperature but in no case could find more than a unique signal for both Me groups. Nor do the phenyl signals in **7** and its derivatives emit information in this regard (Experimental).



Scheme 4.

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†If 2 moles of dienophile have reacted with a *bis*-diene from above (or *both* from below) then the first mole *must* also have reacted from above (or from below).

Finally we report that when the anhydride **9** is heated with *neo*-pentylamine at 80° the dienic imide **20** is obtained and converted as above into the tetraenic **6**. The difference in behavior between **5** and **6** is merely one of (quantitative) degree. Scheme 5 shows that here again two mono-adducts are obtained when **6** is treated with one equivalent of PTD. One of these, **21**, gives the C_{2v} *bis*-adduct **23** as proved by its conversion into **24** by irradiation. The second, **22**, affords the C_s *bis*-adduct, **25**. The only difference is that **25** accompanies the mixture of mono-adducts **21** and **22** as shown.

Here too, we see that the bulky *neo*pentyl group has steered some of the incoming dienophile away from topside attack and some of the product is obtained by some of the dienophile attacking from below. We believe that these cases buttress our thesis regarding secondary orbital control during those Diels-Alder reactions when the CO groups are allowed to express themselves fully without steric interference being superimposed. Even when the latter is brought into play the CO groups apparently are able to honorably hold their own.

In all of our work on this problem we have prepared a large number of substrates which may be viewed as having been formed by the insertion of a ring (3–5 membered) in lieu of the two bridgehead-hydrogens in *cis*-9,10-dihydronaphthalene. We are now going a step further in employing **9** in reaction with derivatives of α-aminoacids. One may thus obtain at one fell swoop compounds having umbrellas of variable cover on the two top faces of the two cyclohexene or cyclohexadiene rings in the propellane substrates and concurrently we obtain chiral propellanes. From our preliminary results we have further tetraenic substrates in which a steric effect is superimposed upon the electronic one in compounds of type 1.[5]

EXPERIMENTAL

11,13 - *Dioxo* - 12 - *phenyl* - 12 - *aza*[4.4.3]*propella* - 3,8 - *diene*, **10**

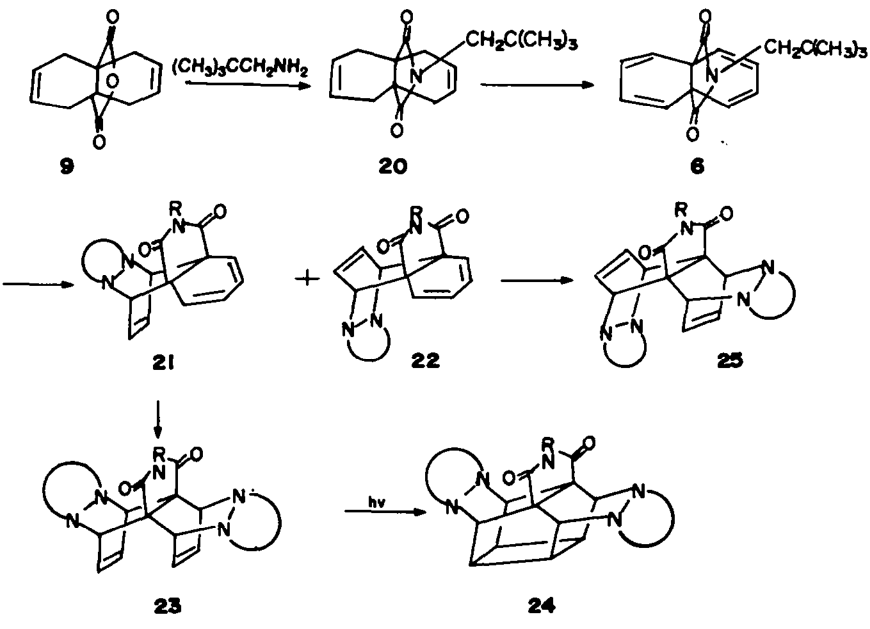
The corresponding dienic anhydride **9**[6] (250 mg) was stirred with freshly distilled aniline (1 ml) at 75° overnight. After cooling to r.t. ether (30 ml) was added and the whole was washed with HCl (10%; 3 × 15 ml). After drying ($MgSO_4$) and removal of solvent **4** was obtained (280 *mg*; 82%). *The analytical sample had* m.p. 129–131° (benzene-hexane). (Found: C, 77.02; H, 6.28; N, 5.06; M.W. 279.1246. $C_{18}H_{17}NO_2$ requires: C, 77.39; H, 6.13; N, 5.01%; M.W. 279.1248). NMR ($CDCl_3$): τ 2.30–2.90 (m, 5 arom H); 4.00 (t, J = 3 Hz, 4 vinylic H); 7.00–8.10 (m, 8 allylic H). IR ($CHCl_3$): 2950, 2850, 1775, 1700 1600 cm^{-1}. MS: M^+, 279 (100); 197 (16); 128 (7); 105 (48).

11,13 - *Dioxo* - 12 - *phenyl* - 12 - *aza*[4.4.3]*propella* - 2,4,7,9 - *tetraene*, **4**

A mixture of **10** (3 g), NBS (4.1 g) dibenzoyl peroxide (20 mg) in CCl_4 (60 ml) was heated under reflux until bromination was complete (30 min). After the usual workup the crude bromide was dissolved in dry benzene (70 ml). Diazabicyclononene (8 g) was added and the whole was stirred overnight at 60°. After cooling to r.t., washing with HCl (10%, 3 × 20 ml), drying and removal of solvent the crude tetraene was obtained (2.1 g). Chromotography on basic alumina (20 g) (Merck, Grade 1) and elution with hexane (9): CH_2Cl_2 (1) afforded **4** (1.2 g; 42%). The analytical sample had m.p. 147–149° (hexane). (Found: C, 77.79; H, 4.82; N, 5.02; M.W. 275.0971. $C_{18}H_{13}NO_2$ requires: C, 78.53; H, 4.76; N, 5.09%; M.W. 275.0946.) NMR ($CDCl_3$): τ 2.30–2.60 (m, 5 arom H); 3.80–4.34 (A_2B_2, 8 vinylic H). IR ($CHCl_3$): 3000, 1775, 1700, 1600 cm^{-1}. MS, M^+, 275 (7); 128 (100); 127 (71); 119 (29).

Diels–Alder reaction of **4**. A soln of **4** (110 mg) in CH_2Cl_2 (2 *ml) was treated with one of PTD* (70 *mg) in the same solvent* (2 ml). After instantaneous reaction and removal of solvent **11** was obtained quantitatively. The analytical sample had m.p. 231–233° (dec, benzene). (Found: C, 68.92, H, 4.09; N, 12.28. $C_{26}H_{18}N_4O_2$ requires: C, 69.32; H, 4.03; N, 12.44%). NMR ($CDCl_3$): 2.57 (s, 5 arom H); 2.63 (s, 5 arom H); 3.34 (t, J = 3 Hz, 2 vinylic H); 3.90–4.10 (m, 4 diene H); 4.67 (t, J = 3 Hz, 2 allylic H). IR ($CHCl_3$): 3000, 1785, 1730, 1600 cm^{-1}. MS: $M^+ -C_{14}H_9N$, 227 (100); 128 (10); 119 (35).

Diels–Alder reaction of **11**. The mono-adduct **11** (45 mg) in CH_2Cl_2 (3 ml) reacted instantaneously with PTD (17.5 mg) in CH_2Cl_2 (2 ml). Removal of solvent afforded quantitatively the *bis*-adduct **12**. Trituration with MeOH gave the pure sample, m.p. 293–294° (dec.) (Found: C, 65.37; H, 3.79; N, 15.39. $C_{34}H_{23}N_7O_6$ requires: C, 65.33; H, 3.71; N, 15.69%). NMR (DMSO-d_6): τ 2.50 (br s, 15 arom H); 3.60 (t, J = 3 Hz, 4 vinylic H); 4.60 (t, J = 3 Hz, 4 allylic H). IR (KBr): 3040, 2980, 1780, 1730, 1600 cm^{-1}. MS: $M^+ -C_{22}H_{14}N_4O_4$, 227 (100); 179 (21); 119 (76).



Scheme 5.

Irradiation of **12**. A soln of **12** (72 mg) in acetone (70 ml) was irradiated in an evacuated tube after degassing using a Rayonet reactor with 3000Å lamps during 30 hr. After removal of solvent, trituration with a little acetone gave the cage product **13** (62 mg, 86%), m.p. 329–331° (Found: M.W. 625.3090. $C_{34}H_{23}N_7O_6$ requires: 625.3120). NMR (DMSO-d_6): τ 2.50 (br s, 15 arom H); 4.23 (s, 4 C$\underline{H}$N); cyclobutyl protons are masked by the water in solvent. IR (KBr): 2960, 1775, 1730, 1600 cm^{-1}. MS: M^+, 625 (0.8); 227 (100); 119 (30).

11, 13 - *Dioxo* - 12 - (2′,6′ - *dimethylphenyl*) - 12 - *aza*[4.4.3]*propella* - 3,8 - *diene*, **14**. The anhydride **9** (12 g) was heated with stirring in 2,6-dimethylaniline (15 ml) at 110° overnight. After cooling to r.t. CH_2Cl_2 (60 ml) was added and the whole was washed with HCl (10%; 3 × 20 ml). After drying ($MgSO_4$) and removal of solvent, crude **14** was obtained (16 g; 89%), m.p. 239–241° (benzene-hexane). (Found: C, 77.97; H, 6.93; N, 4.47; M.W. 307.1592. $C_{20}H_{21}NO_2$ requires: C, 78.14; H, 6.89; N, 4.56%; M.W. 307.1572). NMR ($CDCl_3$): τ 2.87 (s, 3 arom H); 4.00 (t, J = 3 Hz, 4 vinylic H); 7.00–7.87 (m, 8 allylic H); 8.00 (s, 6C$\underline{H}_3$). IR ($CHCl_3$): 2920, 1780, 1710 cm^{-1}. MS: M^+, 307 (100); 253 (72); 252 (90); 225 (14); 131 (14).

11,13 - *dioxo* - 12 - (2′,6′ - *dimethylphenyl*) - 12 - *aza*[4.4.3]*propella* - 2,4,7,9 - *tetraene*, **5**. A mixture of **14** (4.5 g), NBS (5.4 g), dibenzoyl peroxide (20 mg) and CCl_4 (150 ml) was heated until bromination was complete (45 min). After the usual workup (as described for **4**) the crude bromide in dry benzene (100 ml) was stirred with DBN (15 g) overnight at 80°. After workup as above the crude **5** (2.9 g; 65%) was recrystallized, m.p. 201–203° benzene). (Found: C, 78.67; H, 5.75; N, 4.73; M.W. 303.1311. $C_{20}H_{17}NO_2$ requires: C, 79.18; H, 5.65; N, 4.62%; M.W. 303.1260). NMR ($CDCl_3$): τ 2.80 (s, 3 arom H); 3.80–4.27 (m, A_2B_2, 8 diene H); 8.00 (s, 6C$\underline{H}_3$). IR ($CHCl_3$): 2960, 1790, 1680 cm^{-1}. MS: M^+, 303 (10); 147 (47); 129 (100); 127 (52).

Diels–Alder reaction of **5**. General comment: Our experience enables us to tell in an NMR spectrum of a crude product if attack has occurred from above, below, or from both directions. The remaining diene moiety in a monoadduct exhibits a narrow absorption band when attack has occurred from above; it is a typical A_2B_2 absorption. The former was also observed in the N-phenylimide, **4** its N-Me analog, etc.

Immediate reaction occurred when **5** (90 mg) in CH_2Cl_2 (3 ml) was treated with PTD (54 mg) in CH_2Cl_2 (3 ml). After the usual workup the NMR spectrum of the crude product clearly showed that attack had occurred from both directions. Separation was effected by using 9 plates of silica (Merck, 20 × 20 cm, thickness 2 mm) with CH_2Cl_2 as eluant. The mono-adduct **15** (60 mg) isolated had m.p. 265–267° (dec, $CHCl_3$-hexane). Its isomer **16** (65 mg), had m.p. 174–176° (benzene–hexane). Effectively the isomer ratio is 1:1 with 86% recovery from the TLC plates (125 mg from 144 mg used for separation).

Isomer **15**. (Found: C, 69.04; H, 4.86; N, 11.07. $C_{28}H_{22}N_4O_4$ requires: C, 70.28; H, 4.63; N, 11.71%). NMR ($CDCl_3$): τ 2.53 (s, 5 arom H); 2.67 (s, 3 arom H); 3.27 (t, J = 3 Hz, 2 vinylic H); 3.90–4.10 (m, 4 diene H); 4.57 (t, J = 3 Hz, 2 allylic H); 7.80 (s, 3C$\underline{H}_3$); 8.00 (s, $3CH_3$). IR ($CHCl_3$): 2920, 1780, 1720, 1600 cm^{-1}. MS; $M^+ - C_6H_{13}NO_2$, 227 (100); 119 (26).

Isomer **16**. (Found: C, 69.29; H, 4.71; N, 11.60). NMR ($CDCl_3$): τ 2.57 (s, 5 arom H); 2.70 (s, 3 arom H); 3.30 (t, J = 3 Hz, 2 vinylic H); 3.50–4.10 (A_2B_2; 4 diene H); 4.67 (t, J = 3 Hz, 2 allylic H); 7.97 (s, 3C$\underline{H}_3$); 8.06 (s, 3C$\underline{H}_3$). IR ($CHCl_3$): 2940, 1760, 1710, 1600 cm^{-1}. MS: 227 (60); 181 (90); 119 (100).

Preparation of **17**. The reaction between **15** (27 mg) in CH_2Cl_2 (4 ml) and PTD (10 mg) in CH_2Cl_2 (1 ml) requires nearly 1 hr for completion (r.t.) After removal of solvent trituration with MeOH gave the *bis*-adduct **17**, m.p. 333–335° (dec.). (Found: N, 14.69. $C_{36}H_{27}N_7O_6$ requires: N, 14.99%). NMR ($CDCl_3$): τ 2.60 (s, 10 arom H); 2.70 (s, 3 arom H); 3.50 (t, J = 3 Hz, 4 vinylic H); 4.43 (t, J = 3 Hz, 4 allylic H); 7.80 (s, 6 C$\underline{H}_3$). IR (KBr): 2900, 1780, 1720, 1600 cm^{-1}. MS: 227 (78); 181 (90); 119 (100).

Irradiation of **17**. A soln of **17** (30 mg) in acetone (30 ml) was degassed and irradiated as described for **12** for 24 hr. After analogous workup trituration with acetone gave **18** (24 mg; 80%), m.p. > 350°. (Found: M.W. 653.2012. $C_{36}H_{27}N_7O_6$ requires: 653.2022). NMR ($CDCl_3$): τ 2.55 (s, 10 arom H); 2.74 (s, 3 arom H); 4.80 (br s, 4 C$\underline{H}$N); 6.53 (br s, 4 cyclobutane H); 7.83 (s, 6 C$\underline{H}_3$). IR (KBr): 2960, 1770, 1720, 1610 cm^{-1}. MS: M^+, 653 (100); 227 (83); 119 (24).

Preparation of **19**. Reaction of **16** (26 mg) in CH_2Cl_2 (4 ml) with PTD (9 mg) in CH_2Cl_2 (1 ml) also required *ca* 1 hr. Removal of solvent and trituration with MeOH give the pure *bis*-adduct **19**, m.p. 340–342° (dec). (Found: C, 65.68; H, 4.10; N, 14.76; M.W. 653.2045. $C_{36}H_{27}N_7O_6$ requires: C, 66.21; H, 4.17; N, 14.99%; M.W. 653.2022). NMR ($CDCl_3$): τ 2.57 (s, 10 arom H); 2.74 (3 arom H); 3.30 (t, J = 3 Hz, 2 vinylic H); 3.40 (t, J = 3 Hz, 2 vinylic H); 4.30 (t, J = 3 Hz, 2 allylic H); 4.57 (t, J = 3 Hz, 2 allylic H), 7.85 (s, C$\underline{H}_3$); 7.96 (s, 3C$\underline{H}_3$). IR (KBr): 2950, 1770, 1720, 1600 cm^{-1}. MS: M^+, 653 (34); 227 (100); 181 (27); 133 (16); 119 (28).

11,13 - *Dioxo* - 12 - *neopentyl* - 12 - *aza*[4.4.3]*propella* - 3,8 - *diene*, **20**. Prepared as above from **9** (4.0 g) and neopentylamine (6.0 g) in toluene (50 ml) for 2 hr at 80°, then overnight under reflux. After workup as above crude **20** (4.7 g; 63%) was obtained, m.p. 98–100° (hexane). (Found: C, 75.13; H, 8.15; N, 5.12; M.W. 273.1685. $C_{17}H_{23}NO_2$ requires: C, 74.69; H, 8.48; N, 5.12%; M.W. 273.1722). NMR ($CDCl_3$): τ 4.10 (t, J = 3 Hz, 4 vinylic H); 6.70 (s, 2NC$\underline{H}_2$C$(CH_3)_3$); 7.10–8.00 (m, allylic H); 9.17 (s, 9 NCH_2C(C$\underline{H}_3$)$_3$). IR ($CDCl_3$): 2940, 2830, 1770, 1690 cm^{-1}. MS: M^+, 273 (100); 219 (71); 163 (29); 162 (31); 131 (17).

11,13 - *Dioxo* - 12 - *neopentyl* - 12 - *aza*[4.4.3]*propella* - 2,4,7,9 - *tetraene*, **6**. Prepared as above from **20** (400 mg) and NBS (570 mg) in CCl_4 (10 ml) with dibenzoyl peroxide (10 mg). After the analogous workup the crude bromide was heated with DBN (1 g) in dry benzene (15 ml) at 80° overnight. After workup as above crude **6** (255 mg) was purified by TLC on silica (Merck, 20 × 20 cm, 2 mm thick) using acetone (1): hexane (3). Pure **6** (170 mg; 45%) had m.p. 117–119° (hexane). (Found: M.W. 269.1398. $C_{17}H_{19}NO_2$ requires: 269.1415). NMR ($CDCl_3$): τ 3.90–4.40 (m, 8 vinylic H); 6.53 (s, 2NC$\underline{H}_2$ C$(CH_3)_3$); 9.10 (s, 9NCH_2C(C$\underline{H}_3$)$_3$). IR ($CHCl_3$): 2950, 1780, 1700 cm^{-1}. MS: M^+, 269 (16); 144 (27); 127 (100).

Diels–Alder reaction of **6**. The immediate reaction of **6** (108 mg) in CH_2Cl_2 (2 ml) with PTD (70 mg) in CH_2Cl_2 (2 ml) gave a crude mixture which contained the mono-adducts **21** and **22** and *bis*-adduct **25**. Separation by TLC on 4 silica plates (Merck, 20 × 20 cm, 2 mm thick) with acetone (1): hexane (3). Fractions were obtained of **21** and **22** (52 mg; ratio 1:1 by NMR); pure **21** (54 mg); **25** (25 mg), i.e. from 178 mg crude products, 131 mg (75%) was recovered from TLC plates. On the basis of the latter the composition is **21** (61%); **22** (20%); **25** (19%). The isomer **22** was obtained pure by two runs on similar silica plates using hexane (1): CH_2Cl_2 (4).

Mono-adduct **21**. m.p. 145–147° (benzene-hexane). (Found: N, 12.55. $C_{25}H_{24}N_4O_4$ requires: N, 12.61%). NMR ($CDCl_3$): τ 2.57 (s, 5 arom H); 3.34 (t, J = 3 Hz, 2 vinylic H); 4.00–4.14 (m, 4 diene H); 4.70 (t, J = 3 Hz, 2 allylic H); 6.57 (s, 2NC$\underline{H}_2$ C$(CH_3)_3$); 9.07 (s, 2NCH_2C(C$\underline{H}_3$)$_3$). IR ($CHCl_3$): 2960, 1775, 1710, 1600 cm^{-1}. MS: $M^+ - C_{13}H_{15}NO_2$, 227 (100); 161 (54); 119 (32).

Mono-adduct **22**, m.p. 174–176° (benzene-hexane). (Found: C, 67.53; H, 4.59, $C_{25}H_{24}N_4O_4$ requires: C, 67.55; H, 5.44%). NMR ($CDCl_3$): τ 2.50 (5 arom H); 3.37 (t, J = 3 Hz, 2 vinylic H); 3.50–4.10 (m, 4 diene H); 4.70 (t, J = 3 Hz, 2 allylic H); 6.67 (s, NC$\underline{H}_2$ C$(CH_3)_3$); 9.14 (s, NCH_2C(C$\underline{H}_3$)$_3$). IR ($CHCl_3$): 2940, 1780, 1710, 1600 cm^{-1}. MS: 227 (100); 160 (90); 119 (79).

Bis-*adduct* **25**, m.p. 304–306° (dec. benzene-hexane.) (Found: M.W. 619.2196. $C_{33}H_{29}N_7O_6$ requires: 619.2179). NMR ($CDCl_3$): τ 2.53 (s, 10 arom H); 3.30–3.50 (m, 4 vinylic H); 4.43 (t, J = 3 Hz, 2 allylic H); 4.67 (t, J = 3 Hz, 2 allylic H); 6.67 (s, 2NC$\underline{H}_2$ C$(CH_3)_3$); 9.10 (s, 9NCH_2C(C$\underline{H}_3$)$_3$). IR ($CHCl_3$): 2940, 1780, 1715, 1610 cm^{-1}. MS: M^+, 619 (17); 227 (100); 119 (24).

Preparation of **23**. The reaction between **21** (26 mg) in CH_2Cl_2 (2 ml) and PTD (10 mg) in CH_2Cl_2 (1 ml) required 3–4 min for completion. Removal of solvent gave **23** quantitatively, m.p. 282–283° (dec, benzene–hexane). (Found: N, 15.42; M.W. 619.2191. $C_{33}H_{29}N_7O_6$ requires: N, 15.82%; M.W. 619.2179). NMR ($CDCl_3$): τ 2.57 (s, 10 arom H); 3.70 (t, J = 3 Hz, 4 vinylic H); 4.60 (t, J = 3 Hz, 4 allylic H); 6.43 (s, 2NC$\underline{H}_2$C$(CH_3)_3$); 9.00 (s, 9NCH_2C(C$\underline{H}_3$)$_3$). IR ($CHCl_3$): 2950, 1780, 1720, 1600 cm^{-1}. MS: M^+, 619 (9); 227 (100); 181 (48); 161 (42); 119 (62).

Irradiation of **23**. As above, **23** (35 mg) in acetone (40 ml), degassed, Rayonet 24 hr gave **24** (30 mg, 86%), m.p. 323–325°

(dec, acetone). (Found: M.W. 619.2149. $C_{33}H_{29}N_7O_6$ requires: 619.2179). NMR ($CDCl_3$): τ 2.50 (s, 10 arom H); 5.00 (br s, 4 $C\underline{H}N$); 6.43 (s, 2$NC\underline{H}_2$ $C(CH_3)_3$); 6.73 (s, 4 cyclobutane H); 9.10 (s, 9$NCH_2C(C\underline{H}_3)_3$. IR ($CHCl_3$): 2940, 1770, 1720, 1600 cm^{-1}. MS: M^+, 619 (100); 227 (78); 119 (15).

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