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PROPELLANES—XXXVI

REACTIONS OF BRIDGED [10]ANNULENES WITH 4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONES†

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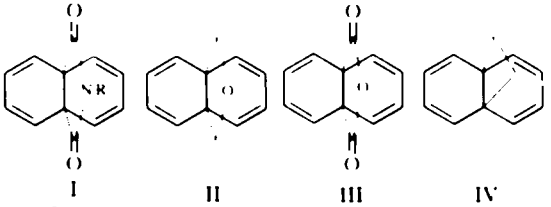
Abstract—1,6-Methano-, 1,6-oxa-, 1,6-imino- and 1,6-methylimino[10]annulene as well as several derivatives of the first-named compound react with 4-substituted-1,2,4-triazoline-3,5-diones to give *mono*- and/or *bis*-adducts. Attack apparently occurs from the side *anti*- to the bridging atom. Mass spectral results are reported for certain mixed di-adducts.

Since we appreciate the fact that bridged [10]annulenes are "open" [4.4.1]propellanes and that [4.4.1]propellanes are "closed" bridged [10]annulenes, we have decided to embark on a joint venture which would utilize these respective substrates for the benefit of increased understanding of both. Thus it has been possible with tetraenic propellanes to obtain *bis*-adducts with certain dienophiles. The fact that Ia is attacked by the dienophile cited in the title from above whilst II is attacked by the same dienophile from below has been explained by involving secondary orbital effects, interaction of carbonyl orbitals of Ia with lone pair orbitals of the dienophile, which stabilizes the transition state for attack from above.[1] Related methylimides are also attacked, apparently for the same reason, exclusively from above.[1] Meanwhile we have found also that Ib and III are attacked exclusively from above.[1] The second equivalent of dienophile usually



I II III IV

a: R = Me
b: R = H

attacks from above (in Ia with a selectivity of 3:1 in favor of attack from above; in II exclusively from above). No propellane substrate has as yet been found in which both equivalents of dienophile attack from below.

It might be expected that in 1,6-methano[10]annulene steric hindrance exerted by the CH_2 hydrogens may cause attack by both moles of dienophile from below, if a *bis*-adduct could in fact be formed. The behavior of 1,6-imino and 1,6-methylimino[10]annulene cannot be predicted with the same degree of certainty. Perhaps certain 11,11 - disubstituted - 1,6 - methano[10]annulenes may interact through secondary orbital effects with the dienophile and attack in such cases may occur from above.

Bridged [10]annulenes have been shown to undergo Diels-Alder reaction with one mole of dienophile.[4] We report herein our results employing 4 - phenyl - 1,2,4 - triazoline - 3,5 - dione as a dienophile of rather higher reactivity. Since the adducts had rather low solubility we used as an additional dienophile the 4-methyl analog; indeed the respective products had relatively greater solubility.

We report herein our results with the parent compounds in the bridged [10]annulene series, i.e. **1**, **4** and **6** containing a CH_2 bridge, the oxa-analog **9** and the imino- and methylimino compounds, **11** and **14**, respectively. Scheme 1 summarizes the results with respect to the carbocyclic starting materials.

It should be noted that in both *bis*-adducts **2a** and **2b** the two cyclopropane protons exhibit a singlet in their NMR spectrum. Furthermore, there is one triplet corresponding to 4 vinylic protons rather than 2 triplets corresponding to 2 pairs of such protons. Similarly there is only one triplet, rather than two, corresponding to 4 allylic CHN protons. It is difficult to conceive of attack of **1** by either of the two dienophiles from above, *syn*- to the sterically hindering methylene bridge. But we are aware that difficulty in conception does not rule out occasional pregnant results. Thus, although we present some evidence below regarding this configurational matter we shall eventually report X-ray structural results which will constitute unequivocal proof. Chemical proof has established the structure of the *mono*-adduct of **1** with maleic anhydride.[4] The dienophile in that case attacks from below but at this juncture this supplies only support by analogy rather than absolute certainty. It is certain, however, that attack of **1**, **4**, and **6** occurs from the *same* direction and that all of the *mono*-adducts represented as **3**, **5** and **7**, respectively, are members of the *same* configurational family. This was shown by reduction of each of these to afford the same perhydro compound **8**. They are in this wise represented

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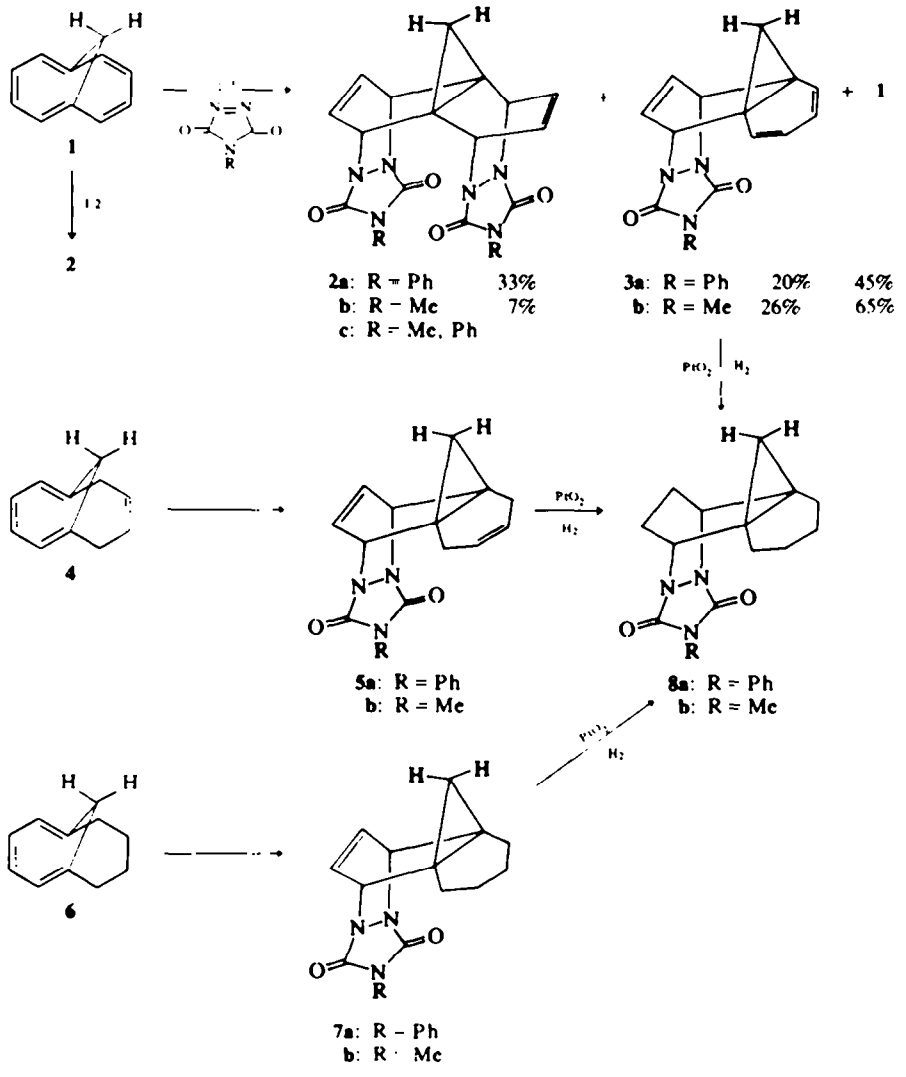


Scheme 1.

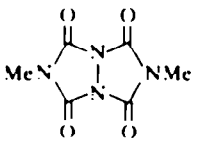
based on the logic which states: If 2 moles of dienophile attack from below then the first mole *must* also have attacked from below.

We had long looked forward to obtaining this type of propellane structure. For I and III had supplied us with *bis*-adducts with the dienophile rings *syn*- to the heterocyclic ring in the propellane precursor.[1] From II, and its sulfur analog[3] and from IV,[5] we had obtained *bis*-adducts in which one of the entering heterocyclic rings was disposed *syn*- with respect to the ether, thioether or cyclobutane ring, the others are *anti*-. In the present paper, apparently, we have for the first time two entering species *anti*- to the resulting cyclopropane ring. We have great expectations for such compounds, which we have already mentioned in print.[6]

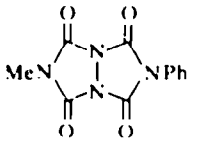
Treatment of **3b** with 4 - phenyl - 1,2,4 - triazoline - 3,5 - dione affords **2c**. However, the technical difficulties encountered in the purification of products were great in view of the type of experiment we wanted to do. We had observed in the mass spectral fragmentations of **2a** and **2b** fragments corresponding to *m/e* 322 and 198, respectively (Scheme 2). We prepared **2c** hoping to obtain only the analogous fragment of *m/e* 260. The Table summarizes the results obtained for different samples of **2c**. It is not surprising that **2a** exhibits only the ion *m/e* 322 as never in its history did it come into contact with 4 - methyl - 1,2,4 - triazoline - 3,5 - dione. Nor is it surprising that **2b** exhibits only the ion *m/e* 198 as never in its history did it come into contact with 4 - phenyl - 1,2,4 - triazoline - 3,5 - dione. Thus only ions of *m/e* 322 or 198, respectively, could be obtained from these whether by an *intra*molecular fragmentation mechanism or an *inter*molecular one.

But when we prepare **2c** from **3b**, the product may be accompanied by some unreacted **3b** which in turn was accompanied by **2b** and recovered **1** during its formation. It is conceivable that **2c** thus contains traces of **2b** and traces of **2a** formed from **1** if this impurity remains in the **3b** starting material. A similar situation may obtain when **2c** is prepared from **3a**. The relative abundances of the ions *m/e* 198, 260 and 322 shown in Table 1, as obtained from various samples of **2c** appear at first sight to indicate that an *inter*molecular mechanism accompanies the *intra*molecular one. We believe that despite difficulties in purification, no more than traces of **2a** and **2b** can accompany **2c**. Even though the statistical factor for *intra*molecular formation of ions of *m/e* 198 and 322 from **2b** and **2a**, respectively is twice that operating of necessity in **2c**, to an ion *m/e* 260, we believe that purification was

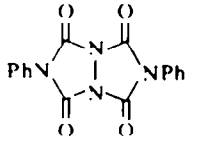
2a → *m/e* *322* (4); 177 (6); 142 (63); 141 (87); 128 (10); 119 (100); 91 (27).
2b → *m/e* 268 (2.7); 254 (1.8); *198* (11); 141 (100); 128 (9.8); 115 (35).
2c → *m/e* M⁺ 430 (0.39); *322* (2.9) *260* (10.4); *198* (3.8) 177 (11); 165 (1.1); 141 (27); 128 (9); 119 (100).



m/e 198



m/e 260



m/e 322

Relative abundances of ions from various samples of **2c**

m/e	198	260	322
	5.3	10	4.7
	6.3	10	2.8
	3.6	10	2.7
	5.5	10	3.5

Scheme 2.

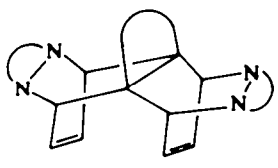
efficient enough to exclude the possibility that relatively large amounts of **2a** and **2b** accompany **2c**.

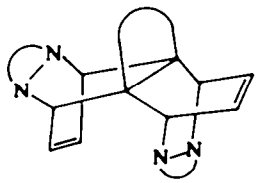
For the purely *inter*molecular reaction, unlikely though it is, one would expect the relative abundance of the ions *m/e* 198, 260 and 322 to be in the ration of 1:2:1. The table gives roughly, very roughly, the appearance of such a ratio. However, in view of the proximity of the triazolinedione rings in the structures, as represented, one would have expected a much higher relative abundance of the unsymmetrical ion, *m/e* 260. Thus these mass spectral results, though interesting, may be taken as proof for the existence of an *inter*molecular reaction rather than that for the configuration shown as evidenced by the expected *intra*molecular reaction. We do not exclude the possibility that some *intra*molecular reaction occurs but if it does it appears to be small. If the reaction had been mainly *intra*molecular we should have expected the data in the table to approximate not 1:2:1 but rather 1:10 or more:1.

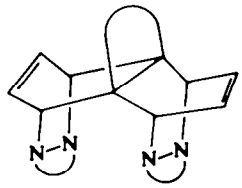
One might explain the statistical ratio obtained by an even less reasonable sequence. The parent ion undergoes retro-Diels–Alder fragmentation to afford both excited N-methyl- and N-phenyl-triazolinedione and these react statistically in the mass spectrometer to give the ions, *m/e* 198, 160, 322. (We have in fact prepared the bicyclic diureide thermally, see Experimental). However, not only is this sequence of consecutive reactions less probable than a more direct attack by an excited ion-molecule of another species but this course is ruled out by other factors. The mono-Diels–Alder adducts clearly show fragmentation patterns (as do the *bis*-adducts) involving retro-Diels–Alder reaction. Thus excited and unexcited dienophile species are formed in the mass spectrometer by this route. Yet *none* of the bicyclic diureide ions is formed. The same holds for the *bis*-adducts of other configurations, i.e. above–above (**A**), above–below (**B**), rather than below–below (**C**). No bicyclic diureide is formed.

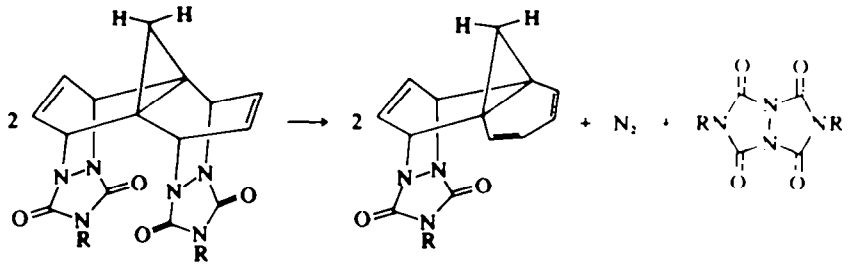
Why should this be? We believe that there is probably more repulsion and discomfort between the two proximate ureide rings in C as compared to the pair made up of one ureide ring and a double bond (B) and between two double bonds (A). We know that A undergoes [2+2]photocycloaddition with great ease.[1] We have also seen frequent *intra*molecular reactions at the centers under discussion in compounds having the B configuration.[2] Thus, C, in the case under discussion undergoes *inter*molecular reaction to relieve its steric and electrostatic discomfort; the formation of the ions corresponding to the bicyclic ureide is proof of this discomfort. One mole of nitrogen must (since we believe in the law of conservation of matter) needs accompany the bicyclic ureide in such an *inter*molecular reaction along with two moles of mono-Diels–Alder adduct (Scheme 3).

The *intra*molecular reaction which is not preferred (if it occurs at all) would give in the above case one mole of 1,6-methano[10]annulene, one mole of bicyclic diureide and one mole of nitrogen. These *bis*-adducts appear to be quite sophisticated in their knowledge of thermodynamics. They must be in order to prefer, in the mass spectrometer under conditions far from optimal for bimolecular reactions, an *inter*molecular rather than the *intra*molecular reaction path. In summary therefore, we take the data in the table as evidence for the previous sentence. Finally, in view of the improbability of the bimolecular reactions discussed above in the mass spectrometer one must consider the possibility that the


A


B


C



Scheme 3.

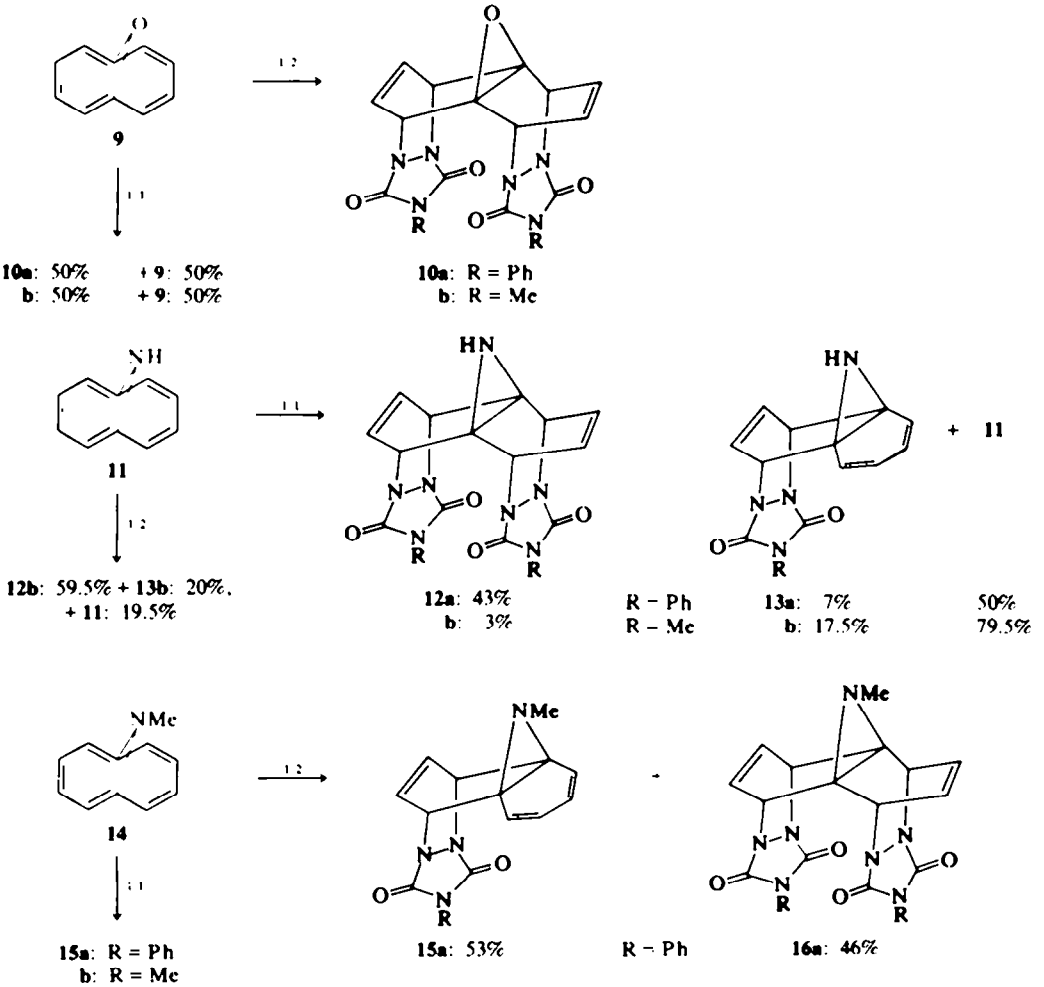
*inter*molecular reaction observed is the prosaic result of thermolysis in the mass spectrometer and not of an excited ion-molecule reaction. That this may indeed be the correct interpretation stems from submitting an equimolar mixture of **2a** and **2b** to electron impact. The ion *m/e* 198 (presumed to be more volatile) appeared earlier than its counterpart *m/e* 322 but none of the mixed ion *m/e* 260 was observed. When the same equimolar mixture was heated to the m.p. (some gas bubbles were observed) and the melt submitted to electron impact, all these ions were observed.

Obtention of unequivocal configurational proof through X-ray crystallography has been undertaken.

Scheme 4 summarizes the results of Diels–Alder reactions of the heterocyclic 1,6-bridged[10]annulenes. Here too, although we do not have the built-in probe extant in the two protons in a 1,6-bridging CH_2 group, the symmetrical NMR spectra of the *bis*-adducts indicate that attack has occurred from the same side, again *presumed* to be from below.

We have no explanation to offer for the observed difference in product distribution obtained from **11** with the dienophiles which differ only in their 4-substituent.

We conclude that the lone pairs on oxygen in **9** and on nitrogen in **11** and in **14** do not appear to change the direction of approach of dienophile as compared to the carbocyclic substrates **1**, **4** and **6**. We are studying 11-substituted and 11,11-disubstituted, both symmetrical and unsymmetrical, 1,6-methano[10]annulene derivatives in order to discover if any of these are capable of exerting



Scheme 4

secondary orbital interactions with the attacking dienophile so as to potentially vary the direction of attack. Similarly we are studying various bridged[14]annulenes mindful of the same goal.

EXPERIMENTAL

IR spectra were measured on a Perkin Elmer model 257 grating spectrometer. NMR spectra were measured on a Varian T-60 spectrometer. Mass spectra were measured on a Varian 711 spectrometer using the direct inlet system. The electron energy was mainatined at 100 eV. Only the major fragments are listed. All m.ps are uncorrected.

Reaction of 1,6-*methano*[10]*annulene and its reduction products with* 4-*phenyl*-1,2,4-*triazoline*-3,5-*dione*

(a) To a soln of **1** (46 mg; 0.32 mmol), in CH_2Cl_2 (5 ml) was added at room temp. a soln of the dienophile (112 mg; 0.64 mmol) in the same solvent (5 ml). The red color disappeared completely after 15 min giving the *bis*-adduct **2a** quantitatively, m.p. 239–241° (chloroform). (Found: C, 65.31; H, 3.92; N, 16.64. $C_{22}H_{20}N_4O_4$ requires: C, 65.84; H, 4.09; N, 17.07%). IR (KBr): 1700, 1490, 1390 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (s, 10 arom H); 3.53 (t, 4 vinylic H); 4.30 (t, 4 allylic CHN); 8.90 (s, 2 cyclopropyl H). MS 322 (4); 177 (6); 142 (63); 141 (87); 128 (10); 119 (100); 91 (27).

To a soln of **1** (72 mg; 0.5 mmol) in CH_2Cl_2 (5 ml) was added at room temp. the dienophile (87 mg; 0.5 mmol) in CH_2Cl_2 (5 ml). The color disappeared after 10 min. After removal of solvent **2a** (66 mg) was precipitated by the addition of chloroform. The residue after evaporation of the mother liquor was dissolved in a small volume of CH_2Cl_2 and hexane was added. The *mono*-adduct **3a** (32 mg) precipitated. The mother liquor still contained starting material **1** (16 mg).

At 0° relatively more *bis*-adduct was obtained. In $CHCl_3$ as solvent, relatively more *mono*-adduct was obtained.

Compound **3a** had m.p. 58–60° (CH_2Cl_2–hexane). (Found: M.W. 317. $C_{18}H_{11}N_3O_2$ requires: 317.33). IR ($CHCl_3$): 1710, 1410 cm^{-1}. NMR ($CDCl_3$): τ 2.55 (s, 5 arom H); 3.65 (t, 2 vinylic H); 3.80 (d, 4 dienic H); 4.75 (t, 2CHN); 8.19 10.08 (ABq, 2 cyclopropane H; J = 6 Hz). MS. M$^+$ 317 (0.6); 141 (100); 128 (7.5); 119 (6); 115 (36).

(b) To **4** (102 mg; 0.78 mmol) in CH_2Cl_2 (2 ml) was added dienophile (135 mg; 0.78 mmol) in CH_2Cl_2 (6 ml) as above. The reaction was instantaneous. Removal of solvent gave the product **5a** quantitatively, m.p. 172–173° (CH_2Cl_2–hexane). (Found: C, 71.24; H, 5.37; N, 13.25; M.W. 319.1285. $C_{19}H_{17}N_3O_2$ requires: C, 71.45; H, 4.93; N, 13.16%; M.W. 319.1311). IR ($CHCl_3$): 1700, 1400 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (s, 5 arom H); 3.70 (t, 2 vinylic H); 4.30 (m, 2 vinylic H); 5.05 (t, 2 CHN); 7.40 (s, 4 allylic H); 9.27, 9.42 (q, 2 cyclopropane H; J = 6 Hz). M.S. M$^+$ 319 (2.5); 144 (30); 143 (43); 142 (25); 141 (23); 129 (100); 128 (66); 119 (47); 91 (32).

(c) To a soln of **6** (94 mg; 0.64 mmol) in CH_2Cl_2 (2 ml) was added as above dienophile (114 mg; 0.64 mmol) in CH_2Cl_2 (4 ml). After instantaneous reaction the solvent was removed, affording **7a** quantitatively, m.p. 182–183° (CH_2Cl_2–hexane). (Found: C, 71.17; H, 6.08; N, 12.46; M.W. 321. $C_{19}H_{19}N_3O_2$ requires: C, 71.01; H, 5.96; N, 13.08%; M.W. 321.37). IR ($CHCl_3$): 1690, 1480 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (s, 5 arom H); 3.88 (t, 2 vinylic H); 5.10 (t, 2 CHN); 7.60–8.90 (m, 8 CH_2); 9.39, 9.60 (q, 2 cyclopropane H, J = 6.5 Hz). MS. M$^+$, 321 (99); 190 (26); 186 (16); 159 (32); 146 (83); 145 (100); 131 (100); 119 (98); 91 (100).

Reaction with 4-*methyl*-1,2,4-*triazoline*-3,5-*dione*

(a) A mixture at room temp. of **1** (56 mg; 0.5 mmol) in CH_2Cl_2 (10 ml) to which was added the N-methyl dienophile (140 mg; 1.0 mmol) in CH_2Cl_2 (40 ml) was allowed to stand at room temp. for 6 hr. Evaporation of solvent gave crude product (198 mg). Extraction with hexane gave unreacted **1**. Extraction with benzene gave *mono*-adduct **3b** (67 mg) and the insoluble *bis*-adduct **2b** (27 mg) (see below). The *mono*-adduct was purified on a preparative silica plate using chloroform as eluant. It had m.p. 239° (benzene–hexane). (Found: C, 65.13; H, 5.13; N, 16.37; M.W. 255.0994. $C_{14}H_{13}N_3O_2$ requires: C, 65.87; H, 5.13; N, 16.46%; M.W. 255.1007). IR ($CHCl_3$): 1705, 1670, 1460 cm^{-1}. NMR ($CDCl_3$): τ 3.75 (t, 2 vinylic H); 3.78 (s, 4 diene H); 4.80 (t, 2 CHN); 7.00 (s, 3NCH$_3$); 8.25, 10.12 (q, 2 cyclopropane H, J = 6 Hz). MS. M$^+$ 255 (6); 141 (100); 128 (11).

The *mono*-adduct (11 mg) and dienophile (8 mg) in CH_2Cl_2 (5 ml) gave after 24 hr the *bis*-adduct quantitatively, m.p. 252–254° identical with that described below.

To a soln of **1** (101 mg; 0.7 mmol) in CH_2Cl_2 (10 ml) was added as above dienophile (158 mg; 1.4 mmol) in CH_2Cl_2 (10 ml). After 30 min the red solution assumed a purple color which disappeared after 2 hr. Evaporation of solvent afforded *bis*-adduct **2b** (263 mg), m.p. 253–254° (ethyl acetate). (Found: C, 54.73; H, 4.53; N, 22.51; M.W. 368.1222. $C_{16}H_{16}N_8O_4$ requires: C, 55.43; H, 4.38; N, 22.81%; M.W. 368.1232). IR ($CHCl_3$): 1710, 1670 cm^{-1}. NMR ($CDCl_3$): τ 3.70 (t, 4 vinylic H); 4.50 (t, 4 CHN); 7.60 (s, 6 NCH$_3$); 9.05 (s, CH$_2$). MS. M$^+$ 368 (2.8); 254 (1); 198 (11); 141 (100); 115 (35).

(b) Instantaneous reaction of **4** (32 mg) in CH_2Cl_2 (5 ml) with dienophile (25 mg) in CH_2Cl_2 (5 ml) gave **5b** (57 mg), m.p. 218–219° (hexane–benzene). (Found: C, 65.42; H, 5.83; N, 16.39; M.W. 257.1187. $C_{14}H_{15}N_3O_2$ requires: C, 65.35; H, 5.88; N, 16.33%; M.W. 257.1165). IR ($CHCl_3$): 1700, 1665, 1460 cm^{-1}. NMR ($CDCl_3$): τ 3.85 (t, 2 vinylic H); 4.30 (m, 2 vinylic H); 5.15 (t, 2 CHN); 7.00 (s, 3 NCH$_3$); 7.40 (m, 4 allylic H); 9.32, 9.47 (q, 2 cyclopropane H, J 6 Hz). MS. M$^+$ 257 (14); 143 (56); 142 (48); 141 (33); 129 (100); 128 (70).

(c) Instantaneous reaction of **6** (31 mg) in CH_2Cl_2 (5 ml) with dienophile (25 mg) in CH_2Cl_2 (5 ml) gave **7b** (58 mg), m.p. 167–168° (hexane). (Found: C, 65.49; H, 6.68; N, 15.62; M.W. 259.1280. $C_{14}H_{17}N_3O_2$ requires: C, 64.84; H, 6.61; N, 16.21%; M.W. 259.1131). IR ($CHCl_3$): 1700, 1660 cm^{-1}. NMR ($CDCl_3$): τ 3.90 (t, 2 vinylic H); 5.20 (t, 2 CHN); 7.0 (s, 3NCH$_3$), 7.80–8.80 (m, 8 CH$_2$); 9.39, 9.64 (ABq, 2 cyclopropane H, J = 6 Hz). MS. M$^+$ 259 (30); 145 (100); 131 (92); 128 (42).

Correlation of configurations

(a) Reduction of **7a** (35 mg) in EtOAc (10 ml) using PtO_2 (3 mg) at m.p. during 3 hr followed by removal of catalyst and solvent afforded the crude product. Chromatography on a preparative silica plate using CH_2Cl_2 as eluant, afforded the perhydro-compound **8a** (31 mg), m.p. 169–170° (CH_2Cl_2–hexane). (Found: C, 70.21; H, 6.64; N, 12.72; M.W. 323.1634. $C_{19}H_{21}N_3O_2$ requires: C, 70.56; H, 6.55; N, 13.06%; M.W. 323.1634). IR ($CHCl_3$): 1680, 1400 cm^{-1}. NMR ($CDCl_3$): τ 2.45 (m, 5 arom H); 5.50 (d, 2 CHN); 7.50–9.00 (m, 12 CH$_2$); 8.95, 9.42 (q, 2 cyclopropane H, J = 6.5 Hz). MS. M$^+$ 323 (14); 268 (100); 149 (19); 119 (5).

(b) Similar reduction of **5a** and similar workup gave **8a**, m.p. 168–169° identical by mixed m.p. and spectroscopically with the above authentic sample. However, the crude reduction product had the following MS. (M$^+$ + 2), 325 (26); M$^+$, 323 (40); 281 (22); 268 (84); 149 (62); 147 (27); 119 (42); 107 (18); 105 (37); 93 (18); 91 (68). After purification as above the molecular peaks were 325 (3) and 323 (100).

(c) Similar reduction of **3a** and similar workup gave **8a**, m.p. 165°, m.m.p. with above product 169°, identical spectroscopically with the authentic specimen. Here too the product of *m/e* 325 was present.

(d) Attempted hydrogenolysis of either bond of the cyclopropane ring in **8a** using the same reduction conditions gave no product of *m/e* 325. Compound **8a** was recovered unchanged.

(e) Similar reduction of **7b** (42 mg) and workup ($CHCl_3$ as eluant) gave **8b** (40 mg), m.p. 93° (hexane). (Found: C, 64.16; H, 7.22; N, 15.89; M.W. 261.1473. $C_{14}H_{19}N_3O_2$ requires: C, 64.34; H, 7.33; N, 16.08%; M.W. 261.1477). IR ($CHCl_3$): 1750, 1670, 1460 cm^{-1}. NMR ($CDCl_3$): τ 5.60 (m, 2 CHN); 6.85 (s, 3NCH$_3$); 8.00–8.90 (m, 14 CH$_2$, CH); 8.95, 9.44 (q, 2 cyclopropane H, J = 7 Hz). MS. M 261 (14); 219 (12); 206 (100); 149 (18).

(f) Similar reduction of **5b** and workup gave **8b**, m.p. 92° identical by m.m.p. and spectroscopically with the above authentic sample. MS (M$^+$ + 2) 263 (6), M$^+$, 261 (37); 219 (33); 206 (100); 149 (52); 147 (18).

(g) Similar reduction of **3b** and workup afforded **8b**, m.p. 92° similarly identical with the authentic specimen. MS. (M$^+$ + 2), 263 (10); M$^+$, 261 (14); 219 (14); 206 (100); 149 (17); 147 (12).

Reduction of **2b**

The *bis*-adduct **2b** (100 mg) in EtOH (1000 ml) was reduced using PtO_2 (20 mg) at atm. p. for 24 hr. Workup as above afforded the tetrahydro derivative (100 mg), m.p. 269° (EtOH). (Found: C, 54.93; H, 4.98; N, 22.60; M.W. 372.1531. $C_{17}H_{24}N_4O_4$ requires: C, 54.83; H, 5.41; N, 22.57%; M.W. 372.1545). NMR ($CDCl_3$): τ 5.20 (m, 4 CHN); 7.00 (s, $3NCH_3$); 8.15 (m, 8 CH_2); 8.55 (m, 2 cyclopropane H). MS. M$^+$, 372 (22); 202 (5); 198 (4); 141 (100); 128 (12).

Preparation of **2c**

(a) Treatment of **3b** (47 mg) with 4-phenyltriazolinedione (27 mg) in CH_2Cl_2 (5 ml) overnight at room temp. gave **2c** (73 mg), m.p. 233–234° (ethanol). (Found: M.W. 430.1374. $C_{22}H_{18}N_6O_4$ requires: 430.1389). NMR ($CDCl_3$): τ 2.45 (br, 5 arom H); 3.65 (2t, 4 vinylic H); 4.40 (2t, 4 CHN); 7.00 (s, 3 NCH_3); 9.00 (s, CH_3). MS. M$^+$, 430 (0.4); 322 (2.85); 260 (10.35); 198 (3.8); 177 (11); 141 (27); 128 (9); 119 (100).

(b) Treatment of **3a** (8 mg) with 4-methyltriazolinedione (6 mg) in CH_2Cl_2 (4 ml) as above, gave an identical product.

Thermolysis of 4-methyl-1,2,4-triazoline-3,5-dione

Heating under reflux of 44 mg in 1,2-dichlorobenzene (20 ml) during 2 hr followed by cooling, removal of the solid product by filtration and washing with EtOH gave the bicyclic ureide (5 mg) m.p. 308° (lit.[a] 303–304°). (Found: M.W. 198.0377. $C_4H_6N_4O_4$ requires: 198.0389). NMR ($CDCl_3$): τ 6.80 (s, NCH_3). MS. M$^+$, 198 (100); 168 (88); 167 (30); 141 (38).

Thermolysis of 4-phenyl-1,2,4-triazoline-3,5-dione

Heating as above of the 4-phenyl derivative (59 mg) and workup gave the bicyclic ureide (5 mg), m.p. 348–350°. (Found: M.W. 322.0718. $C_{16}H_{10}N_4O_4$ requires: 322.0701). NMR ($CDCl_3$): τ 2.55 (br, arom H). MS M$^+$, 322 (22); 119 (53); 57 (100). The ion *m/e* 322 was observed earlier.[a]

Diels–Alder reactions of 1,6-oxa[10]annulene, **9**

(a) *With the N-phenyltriazoline-dione.* The annulene **9** (30 mg) in CH_2Cl_2 (5 ml) was treated with dienophile (73 mg; 1:2) in CH_2Cl_2 (5 ml). Product begins to precipitate after 3 hr. After 24 hr the solid was removed. Only *bis*-adduct **10a** was obtained, m.p. 242–243° (EtOH). Changing reaction conditions did not afford any *mono*-adduct. (Found: C, 62.82; H, 3.84; N, 16.47. $C_{26}H_{18}N_8O_4$ requires: C, 63.15; H, 3.67; N, 17.00%). IR ($CHCl_3$): 1760, 1720, 1400 cm^{-1}. NMR (DMSO-d_6): τ 2.50 (br, 10 arom H); 3.50 (t, 4 vinylic H); 4.30 (t, 4 CHN). MS. 322 (7.3); 319 (15); 177 (17); 172 (5); 157 (5); 144 (4); 132 (12); 128 (3); 119 (100).

(B) *With the N-methyl dienophile.* The annulene **9** (350 mg) in CH_2Cl_2 (30 ml) was treated with the dienophile (274 mg; 1:1) in CH_2Cl_2 (30 ml) and allowed to stand overnight until the color disappeared. After removal of solvent, hexane extracted starting annulene (176 mg). The *bis*-adduct **10b** was obtained (458 mg), m.p. 235–236° (EtOH). (Found: C, 51.64; H, 3.90; N, 22.74; M.W. 370.1018. $C_{16}H_{14}N_8O_4$ requires: C, 51.89; H, 3.81; N, 22.70%; M.W. 370.1025). IR ($CHCl_3$): 1770, 1710, 1650 cm^{-1}. NMR ($CDCl_3$): τ 3.75 (t, 4 vinylic H); 6.45 (t, 4 CHN); 7.00 (s, 6 NCH_3). MS. M$^+$ 370 (37); 257 (100); 198 (34); 172 (27); 165 (14); 157 (12); 144 (51); 128 (20).

Reduction of this *bis*-adduct **10b** (100 mg) in EtOH (1000 ml) using PtO_2 (20 mg) at atm. pressure gave the perhydro-derivative, m.p. 210° (EtOH). (Found: M.W. 374.1302. $C_{16}H_{18}N_8O_4$ requires: 374.1338). NMR ($CDCl_3$): τ 5.10 (m, 4 CHN); 7.00 (s, 6 NCH_3); 8.10 (m, 8 CH_2). MS. M$^+$, 374 (100); 259 (5); 166 (23); 145 (41).

Diels–Alder reactions of 1,6-imino[10]annulene **11**

(a) *With N-phenyl dienophile.* A soln of **11** (52 mg) in CH_2Cl_2 (2 ml) was treated at room temp. with dienophile (62 mg; 1:1) in CH_2Cl_2 (4 ml). The red color disappeared after 1 hr. The *bis*-adduct **12a** precipitated from the mixture (78 mg; 43%). Adding hexane to the mother liquor afforded the crude *mono*-adduct **13a** (8 mg; 7%). The mother liquor afforded recovered **11** (50%). **12a** was obtained quantitatively when **11** was treated with the dienophile in a ratio of 1:2, after 24 hr standing and removal of solvent.

The *bis*-adduct **12a** had m.p. 233–234° (EtOH). (Found: C, 62.80; H, 4.17; N, 19.27. $C_{26}H_{16}N_8O_4$ requires: C, 63.28; H, 3.88; N, 19.87%). IR (KBr): 3320, 1700, 1500, 1400 cm^{-1}. NMR ($CDCl_3$): τ 2.40 (br, 10 arom H); 3.70 (t, 4 vinylic H); 4.45 (t, 4 CHN). MS. 322 (26); 177 (41); 169 (7); 143 (9); 128 (4); 119 (100).

Compound **13a** remained as an oil with IR ($CHCl_3$): 1720, 1400 cm^{-1}. NMR ($CDCl_3$): τ 2.50 (br, 5 arom H); 3.70 (m, 6 vinylic H); 4.30 (m, 2 allylic H). MS. (M$^+$–NH), 303 (5); 227 (9); 177 (50); 169 (16); 143 (53); 128 (85); 119 (73); 93 (100).

(b) *With N-methyl dienophile.* A soln of **11** (50 mg) in CH_2Cl_2 (10 ml) was treated with dienophile (79 mg; 1:2) in CH_2Cl_2 (2 ml). The color disappeared after 24 hr. After removal of solvent the residue was extracted with hexane which dissolved **11** (10 mg; 20%). The insoluble material was treated with EtOAc which dissolved the *mono*-adduct (21 mg), leaving insoluble *bis*-adduct (80 mg).

The *bis*-adduct **12b** had m.p. 223–225° (EtOAc–hexane). (Found: M.W. 369.1170. $C_{16}H_{15}N_7O_4$ requires: M.W. 369.1184). IR ($CHCl_3$): 3300, 1710, 1670, 1460 cm^{-1}. NMR ($CDCl_3$): τ 3.70 (t, 4 vinylic H); 4.45 (t, 4 CHN); 7.0 (s, 6 NCH_3); 8.50 (br, NH, disappears in D_2O). MS. M$^+$, 369 (3.2); 256 (8); 198 (40); 143 (56); 129 (100).

The *mono*-adduct **13b** had m.p. 175–176° (EtOAc–hexane). (Found: M.W. 256. $C_{11}H_{12}N_4O_2$ requires: 256.09). IR ($CHCl_3$): 1760, 1710, 1460 cm^{-1}. NMR ($CDCl_3$): τ 3.40–4.00 (m, 6 vinylic H); 4.70 (m, 2CHN); 7.00 (s, 3 NCH_3). MS. M$^+$, 256 (6); 143 (45), 128 (60); 114 (100).

Diels–Alder reactions of 1,6-methylimino[10]annulene, **14**

(a) *With N-phenyldienophile.* The annulene **14** (30 mg) in CH_2Cl_2 (5 ml) was treated with dienophile (33.5 mg 1:1) in CH_2Cl_2 (10 ml) at room temp. The red color disappeared after 1 hr. The *mono*-adduct **16a** was obtained quantitatively, m.p. 140–142° (CH_2Cl_2–hexane). (Found: C, 68.37; H, 4.88; N, 16.93; M.W. 332.1269. $C_{19}H_{16}N_4O_2$ requires: C, 68.66; H, 4.85; N, 16.86%; M.W. 332.1272). IR ($CHCl_3$): 1720, 1410 cm^{-1}. NMR ($CDCl_3$): τ 2.60 (s, 5 arom H); 3.70 (t, 2 vinylic H); 3.35, 3.90 (m, 4 dienic H); 3.70 (t, 2 vinylic H); 4.75 (t, 2 CHN); 8.55 (s, 3 NCH_3). MS. M$^+$ 332 (46); 177 (1); 157 (10); 128 (100).

Reaction of **14** (21 mg) with dienophile (47 mg; 1:2) as above in CH_2Cl_2 gave after 72 hr *bis*-adduct **15a** (39 mg; 53%) which ppted from the reaction mixture. Hexane precipitated *mono*-adduct **16a** (22 mg; 43%) from the mother liquor, identical with above.

The *bis*-adduct **15a** had m.p. 115–117° (CH_2Cl_2). The compound is thermally very sensitive. IR ($CHCl_3$): 1720, 1400 cm^{-1}. NMR ($CDCl_3$): τ 2.55 (10 arom H); 3.65 (t, 4 vinylic H); 4.35 (t, 4 CHN); 7.35 (s, 3 NCH_3). MS. 322 (12); 177 (46); 128 (11); 119 (100).

(b) *With N-methyl dienophile.* The annulene **14** (30 mg) and dienophile (43 mg; 1:2) in CH_2Cl_2 gave the crude product after 6 days, when the color disappeared, after removal of solvent. Treatment with ethyl acetate gave insoluble *bis*-adduct **15b** (5 mg; 7%). The solvent was removed and the residue taken up in benzene. Hexane was added and the ppt was removed. The *mono*-adduct **16b** (47 mg; 93%) was obtained from the mother liquor.

The *bis*-adduct **15b** had m.p. 183–184° (EtOAc–hexane). It is very sensitive thermally. NMR ($CDCl_3$): τ 3.80 (t, 4 vinylic H); 4.55 (t, 4 CHN); 7.05 (s, 6 NCH_3); 7.30 (s, 3 NCH_3). MS. M$^+$ of *mono*-adduct, 270 (4); 198 (3); 157 (11); 144 (7); 143 (5); 142 (5); 128 (100).

The *mono*-adduct **16b** was an oil. (Found: M.W. 270.1103. $C_{14}H_{14}N_4O_2$ requires: 270.1116). IR ($CHCl_3$): 1720, 1460 cm^{-1}. NMR ($CDCl_3$): τ 3.20–4.00 (m, 6 vinylic H); 4.85 (t, 2 CHN); 7.00 (s, $3NCH_3$); 8.60 (s, 3 NCH_3). MS. M$^+$ 270 (34); 213 (32); 171 (75); 169 (2); 165 (3); 157 (84); 144 (49); 143 (35); 142 (38); 128 (100).

When a ratio of 1:1 is used between the reactants only recovered annulene and *mono*-adduct could be obtained after 24 hr.

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