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PROPELLANES–LI. DIELS–ALDER REACTIONS OF 12-METHYL-12-AZA[4.4.3] PROPELLA-2,4,7,9-TETRAENE WITH NITROSO-AROMATIC DIENOPHILES†

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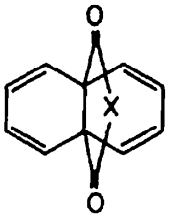
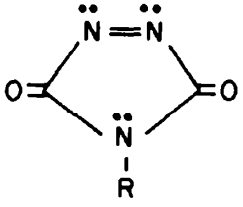
Abstract—Regiospecificity in attack of the title-*bis*-diene by aromatic nitroso compounds as dienophilic components is lower than that of other dienophiles of the triazolinedione type.

In our survey of reactions of propellanes containing CO groups capable of guiding high regiospecific "homing-in" of dienophiles capable of interacting with these groups through secondary orbital interactions, we have described many such cases of π^* (LUMO) interactions of the CO's of compounds of type **1** with the N-antisymmetric combination of lone pair orbitals (HOMO) in dienophiles of type **2**.[1] When the CO groups were missing from **1** in part or totally, the secondary orbital interaction was much lowered or entirely absent.[2] Similarly, if lone pair orbitals were missing at positions 1 and 2 of the dienophile **2**, i.e. the $-\ddot{N}=\ddot{N}-$ bond was replaced (through employing carbon-dienophiles) by a $-CH=CH-$ bond, secondary orbital interaction with compounds of type **1** is, of course, impossible, with concomitant dramatic change in the mode of attack and the relative configuration of the product as compared to attack by dienophiles of type **2**. Thus, for example, when **1**, X=NMe is treated with **2**, R=Me, the exclusive product which could be isolated is **3** whereas **1** with N-methylmaleimide affords exclusively **4**.[3] In the former case, due to secondary orbital interaction of the type described **2** attacks **1** from the side *syn*- with respect to its hetero-ring. In the latter case where such attractive interaction is not possible, steric repulsion causes the formation of the product via attack anti- to the hetero-ring of **1**.



1, X=O, NH, NR

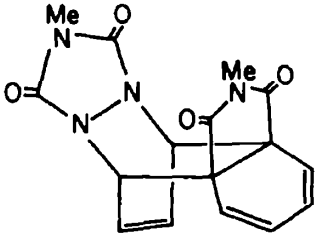


2, R=Me, Ph

In either case, however, the dienophile is symmetric with respect to its reacting double bond. We wondered how the regiospecificity of attack might be affected when such symmetry of the reacting double bond is absent in the dienophile and therefore reacted **1**, X=NMe, first with nitrosobenzene, then with substituted nitrosobenzenes, **5**.

Calculations were carried out for the products of a conceptual Diels–Alder reaction between **1**, X=NH and H−N=O, the four compounds A-D, using the MINDO/3 method. Considering that the error limits for this method is ±5 kcal/mol it is clear that the energy differences between all four compounds is too small to be of any significance.

The feel of the experimental results was no different. Whilst **2** (whether R=Me of Ph) reacts with **1** (X=NMe) to afford exclusively *syn*-attack with



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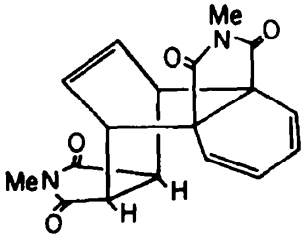

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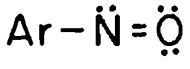

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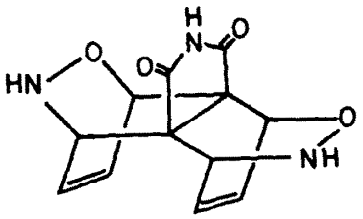
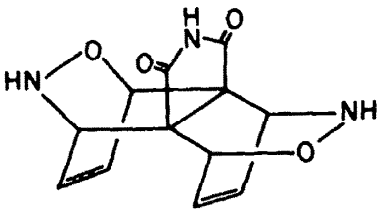
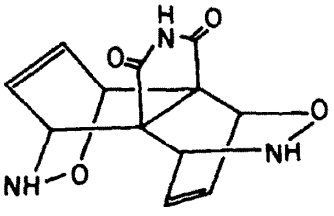
†Part L. M. Kaftory, M. Peled and D. Ginsburg, *Helv. Chim. Acta* **62**, 1326 (1979).



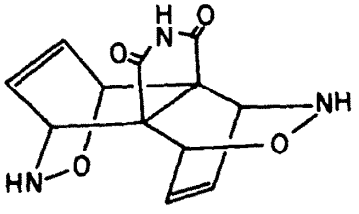
A -24.580 Kcal/mol



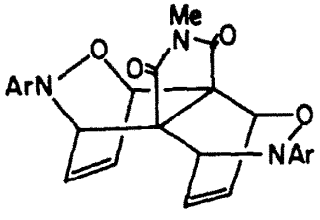
B -24.685 Kcal/mol



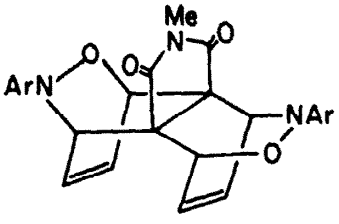
C -24.484 Kcal/mol



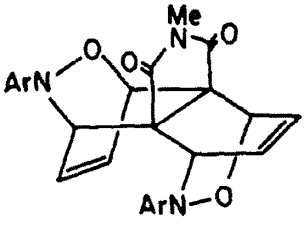
D -24.720 Kcal/mol



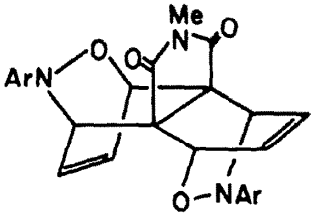
6 h → h
syn – syn



7 h → t
syn – syn



8 h → h
syn – anti



9 h → t
syn – anti

Ar = C_6H_5, p-BrC_6H_4, p-ClC_6H_4

respect to the hetero-ring,[2a] the reaction of nitrosobenzene itself or substituted nitrosobenzenes **5** with the same dienic component **1** gives both *syn* and *anti* products in the ratio of 2:1. And as may be surmised from structures A-D, there are in analogy to the calculated structures of **1** (X=NH) and hyponitrous acid, HNO, 4 possible structures for *bis*-adducts of **5** with **1** (X=NMe); these are **6** ("head to head"), **7** ("head to tail") as *syn-syn*-isomers and **8** ("head to head") and **9** ("head to tail") as *syn-anti*-isomers. We rule out the two further possibilities, head to head and head to tail for the *anti-anti*-possibilities as we have in our, by now large, experience with such derivatives never obtained *anti-anti*-isomers for such propellanes. Only when the propellane derivatives stem from the (methano, oxa or imino)-bridged-[10]-annulene series can such configurational isomers be obtained,[4] but we have not prepared their analogous adducts with aromatic nitroso compounds.

We have shown that singlet oxygen attacks dienic propellanes from the side *syn* to hetero-ring.[5] Thus our nitroso-dienophiles, formally intermediate in structure between triazolinediones and singlet oxygen not only exert their statistical right to give h → h and h → t *bis*-adducts but they afford *anti*-attack in addition to the expected *syn*-attack. The reason for this difference in behavior is not clear at this time.

Since it was extremely difficult to purify the isomer mixtures obtained from nitrosobenzene itself, substituted nitrosobenzenes were invoked. This helped somewhat albeit the products tend to decompose during thin layer chromatography and elution from the plates. Since the mono-adducts could not be separated we resorted to work with *bis*-adducts even though this raises the matter of possible configurational isomers from 2 to 4. The *syn-syn-bis*-adducts are more stable than their *syn-anti* brethren. Fortunately it turned out to be possible to determine the isomer ratio through the criterion of NMR spectroscopy and eventually ^{13}C-high resolution spectroscopy indeed confirmed the presence of all 4 isomers.

NMR spectroscopy was of crucial importance in unravelling the structures of the products formed in the reaction of **1** (X=NMe) with p-bromonitrosobenzene. The proton spectrum of the crude reaction product already indicated the formation of *bis*-adducts and the presence of a mixture of isomers. After thin layer chromatography two non-crystalline fractions A and B were obtained which were subjected to high resolution ^{13}C spectroscopy at 25.2 and 50.3 MHz ($CDCl_3$, δ(TMS) = 0). These spectra exhibit clearly separated regions for the resonances of N-Me carbons (25–26 ppm), quaternary bridgehead carbons (48–54 ppm), nitrogen bearing tertiary carbons (56–62 ppm), oxygen bearing tertiary carbons (69–72 ppm), olefinic carbons (121–131 ppm), and of carbonyl carbons (176–178 ppm). In addition the typical resonance pattern for the *p*-disubstituted aromatic ring can be identified.

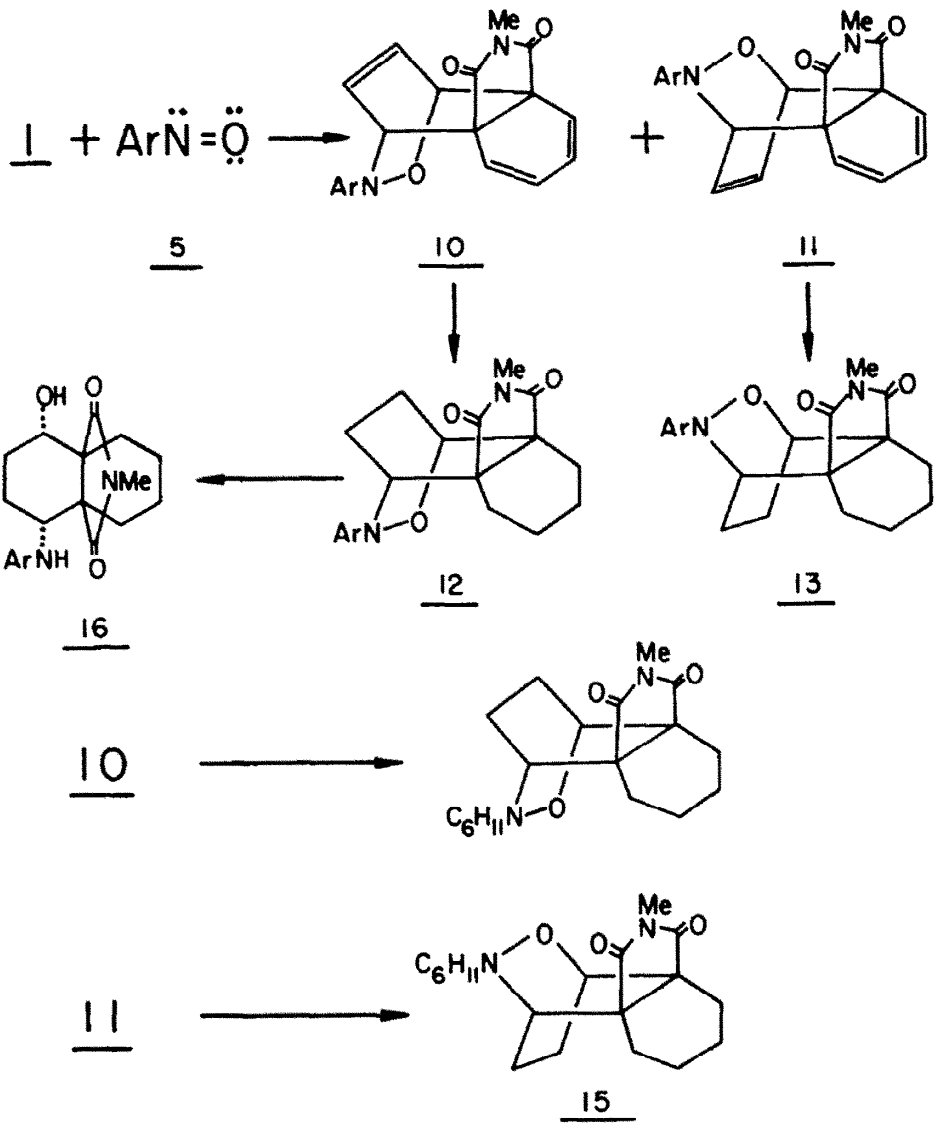
For fraction A the number of lines and their relative intensities observed under proton noise decoupling conditions in the respective regions correspond to a mixture (approx. 1:1) of *syn/anti* isomers ("head to tail" **9** and "head to head" **8**). For example, there are four quaternary resonances, two doublets in the CH–N and one doublet and a single line of double itensity in the CH–O region, as expected for two unsymmetrical adducts. The doublets with a large splitting can be assigned to the CH–O and CH–N carbons associated with the *syn* oriented N–O group since, as suggested by models, only these carbons are also under the influence of the *anti* oriented N–O group. In the olefinic region two well separated groups of four lines each are observed which, as shown further below, can be assigned to the resonances of the *syn* oriented (122–125 ppm) and *anti* oriented (130–131 ppm) double bonds. The presence of a mixture of isomers manifests itself also in a doublet splitting of the aromatic and carbonyl carbons. The N-resonance is not split. An assignment, however, of the doublet components to the "head to head" and "head to tail" isomers is not possible.

In the analysis of the ^{13}C spectrum of fraction B, for which one or both *syn/syn* adducts have to be expected, it is helpful to consider the number of resonances for the "head to tail" isomer **7** (C_2-symmetry) and the "head to head" isomer **6** (S_2-symmetry). H/t: 1 CO, 2 CH=, 1 CH–O, 1 CH–N, 1 C_q and 1 N–CH_3. H/h: 2 CO, 2–CH=, 1 CH–O, 1 CH–N, 2 C_q and 1 N–CH_3. The spectrum obtained at 50.3 MHz clearly shows the presence of both isomers in a ratio close to 1:1 and with all lines resolved, but in addition exhibits a discrete number of additional lines of comparable intensity. From these extra lines one CH–O, one CH–N and six olefinic carbon resonances suggest that the additional component might be the mono-*syn* adduct **11**. This was indeed confirmed by comparison with the spectrum of an authentic sample of **11**. With the exception of the quaternary resonance of the "head to tail" *syn/syn* isomer **7**, which shows a line of twice the intensity of the two quaternary resonances of the "head to head" *syn-syn* isomer **6**, an assignment of individual lines to these two isomers is again not possible. The spectrum of the mono-*syn* adduct **11** permits further assignments of the olefinic carbon resonances in the *syn/anti* and *syn/syn* adducts. In **11** the four carbons of the diene fragment appear at lower frequency (121.3–124.5) than the two carbons of the isolated *anti* oriented double bond (128.8, 131.0 ppm), in agreement with the data of related trienic propellanes.[6] The resonances of the *anti* oriented double bonds in the *syn/syn*- and *syn/anti* adducts also appear at 128–129 ppm and 130–131 ppm, respectively.

Our product mixtures are reminiscent of cases in which the nitroso moiety has been modified by incorporation in the benzonitrile-oxide system[8] or in nitrones.[9] In these cases the mixtures obtained are at least as complex as ours.

Many unsuccessful attempts were made to obtain crystals suitable for X-ray structural determinations. When these failed, we attempted variegated hydrogenolysis of the N=O group in our mono adducts and *bis*-adducts in the hope that transannular reactions between amino or hydroxyl groups particularly in the cases of **6** and **7** would afford structural information. Even the then unpublished procedure kindly disclosed by Dr. G. Keck of the University of Utah, Salt Lake City did not lead to meaningful results in our hands.[7] Several such examples are nevertheless recorded in the experimental section.

The two possible mono-adducts are shown in Scheme 1. Their various reduction products are also shown in the scheme.



Scheme 1.

EXPERIMENTAL

IR spectra were recorded using a Perkin-Elmer 237 spectrometer. NMR spectra were recorded on a Varian T-60 or a Bruker WP-60 instrument and high resolution mass spectra on a Varian MAT 711 spectrometer. Mp's are uncorrected. Chromatographic separation of products was carried out on preparative silica plates (20 × 20 cm; Merck Darmstadt).

Reaction of **1** (X=NMe) *with nitrosobenzene*

(a) A soln of the methylimide (304 mg; 1.4 mmol) and PhNO (160 mg; 1.5 mmol) in CH_2Cl_2 (20 ml) was allowed to stand at room temp for 48 hr. NMR spectroscopy showed the product mixture to be composed of *syn*:*anti* product (2:1). Precipitation with EtOAc afforded **9**, Ar=Ph, the *syn* mono-adduct. The crystalline product (68 mg) had m.p. 158–160° (EtOH). (Found: C, 70.94; H, 4.86; N, 8.75. $C_{19}H_{16}N_2O_3$ requires: C, 71.24; H, 5.03; N, 8.75%). IR ($CHCl_3$): 1780, 1700, 1600, 1460, 1380, 1290 cm^{-1}. NMR ($CDCl_3$): τ 2.60–3.30 (m, 5 arom H); 3.30–3.90 (m, 2 vinylic H); 4.20 (m, 4 dienic H); 5.00 (dd, 1 H, CHO); 5.30 (dd, 1 H, CHN); 6.85 (s, 3 H, NCH_3). MS (m/e): 213 (2.3); 161 (26); 159 (24.3); 131 (19); 130 (100); 128 (86).

After purification in many neutral alumina thin layer plates using chloroform (1): benzene (10) the *anti* mono-adduct **10**, Ar=Ph (26 mg) was obtained, m.p. 124–125° (benzene-hexane). (Found: C, 70.42; H, 5.29; N, 7.61%). IR ($CHCl_3$): 1760, 1700, 1590, 1440, 1380, 970 cm^{-1}. NMR ($CDCl_3$): τ 2.60–3.10 (m, 5 arom H); 3.30–4.20 (m, 6 H, vinylic + dienic): 5.20 (m, 2 H, CHO, CHN); 6.90 (s, 3 H, NCH_3) MS (m/e): 161 (28); 159 (29); 131 (13); 130 (100); 128 (35)

(b) A soln of methylimide (532 mg; 2.5 mmol) and PhNO (528 mg; 5 mmol) in CH_2Cl_2 (100 ml) was set aside at room temp for 6 days. Tlc afforded an oily mixture of **6** + **7** (71 mg) which eventually crystallized, m.p. 88–89° (hexane). (Found: C, 69.79; H, 5.05; N, 9.14. $C_{25}H_{21}N_3O_4$ requires: C, 70.24; H, 4.95; N, 9.83%). IR ($CHCl_3$): 1780, 1700, 1590, 1480, 1440, 1380, 1300, 910 cm^{-1}. NMR ($CDCl_3$): τ 2.50–3.10 (m, 10 arom H); 3.70 (m, 2 vinylic H); 4.15 (m, 2 vinylic H); 4.90 (m, 2 H, CHO); 5.20 (m, 2 H, CHN); 6.85 (s, 3 H, NCH_3). MS (*m/e*): 161 (22); 159 (19); 131 (21); 130 (100); 128 (60).

A mixture of **8** + **9** was obtained as an oil (45 mg) (as well as a fraction of material which could not be further resolved). IR

($CHCl_3$): 1780, 1700 cm^{-1}. NMR ($CDCl_3$): τ 2.50–3.10 (m, 10 arom H); 3.20–4.00 (m, 4 vinylic H); 4.60 (m, 1 H, CHO); 4.90 (m, 2 H, CHO, CHN); 5.20 (m, 1 H, CHN); 7.00 (s, 3 H, NCH_3). MS (m/e): 217 (6); 161 (100); 159 (24); 132 (16); 130 (69); 128 (19).

Reaction with p-*chloronitrosobenzene*

(a) A soln of methylimide (520 mg; 2.45 mmol) and dienophile (355 mg; 2.5 mmol) in CH_2Cl_2 (50 ml) was set aside at room temp for 48 hr. NMR spectroscopy showed that the crude product mixture (880 mg) was composed of *syn* (**2**): *anti* (**1**) isomers. The *syn* mono-adduct **11**, Ar=pClC_6H_4 (240 mg) was insoluble in EtOAc, m.p. 185–187° (EtOAc). (Found: C, 64.65; H, 4.01; N, 7.63. $C_{19}H_{15}N_2O_3Cl$ requires: C, 64.29; H, 4.26; N, 7.89%). IR ($CHCl_3$): 1780, 1700, 1580, 1450, 1380, 1290, 970 cm^{-1}. NMR ($CDCl_3$): τ 2.70, 3.30 (AB, 4 arom H); 3.20–4.00 (m, 2 vinylic H); 4.20 (m, 4 dienic H); 5.00 (dd, 1 H, CHO); 5.30 (dd, 1 H, CHN); 6.92 (s, 3 H, NCH_3). MS (*m/e*): 193 (48); 166 (42); 164 (100); 161 (52).

The *anti* mono-adduct **10**, Ar=pClC_6H_4, was crystallized (111 mg), m.p. 152–153° (CCl_4-hexane). In addition fractions of *syn* + *anti* products (191 mg) and starting tetraene (210 mg) were obtained. (Found: C, 63.69; H, 4.14; N, 7.50). IR ($CHCl_3$): 1770, 1690, 1440, 1380, 1290 cm^{-1}. NMR ($CDCl_3$): τ 2.70, 3.20 (AB, 4 arom H); 3.50–4.20 (m, 6 H, vinylic + dienic); 5.10 (dd, 1 H, CHO); 5.30 (dd, 1 H, CHN); 7.07 (s, 3 H, NCH_3). MS (*m/e*): 193 (34); 166 (34); 164 (100); 161 (94).

(b) The *syn* mono-adduct (85 mg) was reacted with excess dienophile in CH_2Cl_2 (20 ml) for 6 days at room temp. The product (142 mg) appeared to contain a single *bis*-adduct of the *syn-syn* type, m.p. 134–135° (benzene-hexane). IR ($CHCl_3$): 1780, 1700, 1480, 1440, 1380, 990 cm^{-1}. NMR ($CDCl_3$): τ 2.65, 3.30 (AB, 8 arom H); 3.65 (m, 2 vinylic H); 4.10 (m, 2 vinylic H); 4.90 (m, 2 H, CHO); 5.20 (m, 2 H, CHN); 6.90 (s, 3 H, NCH_3). MS (*m/e*): 164 (20); 161 (17); 140 (100).

(c) When the crude mixture of mono-adducts (part a) above) was treated with an excess of the same dienophile in CH_2Cl_2 for 6 days at room temp and the whole was separated on a prep silica plate using hexane (45 ml) and EtOAc (30 ml) the *syn-anti bis*-adduct(s) was obtained as an oil. IR ($CHCl_3$): 1780, 1690, 1480, 1440, 1380, 1300, 1100 cm^{-1}. NMR ($CDCl_3$): τ 2.70, 3.20 (AB, 8 arom H); 3.30–4.30 (m, 4 vinylic H); 4.70 (m, 1 H, CHO); 5.00 (m, 2 H, CHO, CHN); 5.30 (m, 1 H, CHN); 7.08 (s, 3 H, NCH_3). Ms (m/e); 379 (21); 374 (21); 343 (25); 294 (28); 185 (39); 164 (20); 161 (55); 151 (100).

Reaction with p-*bromonitrosobenzene*

(a) A soln of methylimide (221 mg; 1 mmol) and dienophile (227 mg; 1.22 mmol) in CH_2CH_2 (20 ml) was set aside for 48 hr at room temp. The crude product (433 mg) was again shown (NMR) to consist of a *syn*:*anti* mixture of *ca* 2:1. EtOAc does not dissolve the *syn*-isomer which was thus obtained (230 mg) after separation from a fraction (195 mg) of isomer mixture. The *syn*-product **11**, Ar=pBrC_6H_4, had m.p. 193–194° (EtOAc). (Found: C, 56.83; H, 3.44; N, 6.49; M.W. 398.0282. $C_{19}H_{15}N_2O_3Br$ requires: C, 57.15; H, 3.78; N, 7.01%; M.W. 398.0660). IR ($CHCl_3$): 1770, 1700, 1480, 1440, 1380, 920 cm^{-1}. NMR ($CDCl_3$): τ 2.40, 3.40 (AB, 4 arom H); 3.10–3.90 (m, 2 vinylic H); 4.25 (m, 4 dienic H); 5.00 (dd, 1 H, CHO); 5.30 (dd, 1 H, CHN); 6.90 (s, 3 H, NCH_3). MS (*m/e*): M^+, 398 (0.6), 238 (18), 209 (96); 207 (100); 161 (42).

The *anti*-product **10**, Ar=*p*-BrC_6H_4, was separated on prep. silica plate using hexane and EtoAc; the upper third of the band was taken (from a batch using 540 mg starting tetraene, 46 mg pure *anti*-product was isolated). The *anti*-product had m.p. 152–153° (benzene-hexane). (Found: C, 56.39; H, 3.49; N, 6.38). IR ($CHCl_3$): 1770, 1690, 1480, 1440, 1380, 1290 cm^{-1}. NMR ($CDCl_3$): τ 2.40, 3.30 (AB, 4 arom H); 3.00–4.20 (m, 6 H, vinylic + dienic); 5.10 (dd, 1 H, CHO); 5.30 (dd, 1 H, CHN); 7.02 (s, 3 H, NCH_3). MS (*m/e*): 238 (20); 236 (21); 209 (83); 207 (73); 161 (100).

(b) The above *syn*-monoadduct (96 mg) was reacted with excess dienophile in CH_2Cl_2 (20 ml) for 6 days at room temp. Only the *syn-syn*-adduct appears to have formed, m.p. 128–130° (benzene). IR ($CHCl_3$): 1780, 1700 cm^{-1}. NMR ($CDCl_3$): τ 2.45, 3.40 (AB, 8 arom H); 3.65 (m, 2 vinylic H); 4.10 (m, 2 vinylic H); 4.90 (t, 2 H, CHO); 5.30 (t, 2 H, CHN); 6.90 (s, 3 H, NCH_3). MS (*m/e*): 186 (100); 184 (95); 181 (33); 170 (44); 161 (43).

(c) A mixture of the two mono-adducts (part a) above; 155 mg) was treated with an excess of dienophile in CH_2Cl_2 (20 ml) for 4 days at room temp. Chromatography on a prep silica plate using benzene as eluent afforded in addition to the syn-syn-bis adduct just described (69 mg) and a fraction containing a mixture of the *bis*-adducts (192 mg), the *syn-anti-bis*-adduct (74 mg), m.p. 123–125° (benzene-hexane). (Found: C, 51.00; H, 3.75; N, 6.77. $C_{38}H_{38}N_4O_8Br_2$ requires C, 51.13; H, 3.27; N, 7.18%). IR ($CHCl_3$): 1770, 1700 cm^{-1}. NMR ($CDCl_3$): τ 2.45, 3.30 (AB, 8 arom H); 3.30–4.20 (m, 4 vinylic H); 4.60 (m, 1 H, CHO); 5.0 (m, 2 H, CHO, CHN); 5.30 (m, 1 H, CHN); 7.10 (s, 3 H, NCH_3). MS (*m/e*): 238 (12); 209 (18); 207 (16); 161 (100).

Catalytic reduction of mono-adduct mixture from p-*bromonitrosobenzene*

(a) The 2:1 mixture described in part (a) above (144 mg) was reduced in EtOH (50 ml) at 1 atm H_2 using PtO_2 at room temp. After 1 hr 40 ml H_2 had been taken up. Filtration of catalyst and removal of solvent gave the crude product (137 mg).

This consisted of two hexahydro derivatives of the two configurationally different mono-adducts and apparently the octahydro-derivative of the starting propellane tetraene which must have formed first by a retro-Diels-Alder reaction followed by hydrogenation. Separation on a prep silica plate using chloroform as eluent gave *anti*-hexahydro-isomer, **12** (35 mg), *syn*-hexahydro-isomer, **13** (60 mg) and the third product (39 mg).

Isomer **12** had m.p. 142–143° (benzene-hexane). (Found: N, 6.47, M.W. 406.0718. $C_{19}H_{21}N_2O_3Br$ requires: N, 6.91%, M.W. 406.0716). IR ($CHCl_3$): 1780, 1705, 1500, 1000 cm^{-1}. NMR ($CDCl_3$): τ 2.55, 3.00 (AB, 4 arom H); 5.95 (m, 1 H, CHO); 6.30 (m, 1 H, CHN); 6.90 (s, 3 H, NCH_3); 7.40–8.90 (m, 12 H, CH_2). MS (*m/e*): M^+, 406 (100); 404 (93); 225 (6); 223 (6); 183 (21); 181 (32).

Isomer **13** had m.p. 201–202° (benzene-hexane). (Found N, 6.84; M.W. 406.0670). IR ($CHCl_3$): 1780, 1710, 1500, 1080 cm^{-1}. NMR ($CDCl_3$): τ 2.60, 3.05 (AB, 4 arom H); 5.70 (m, 1 H, CHO); 6.15 (m, 1 H, CHN); 6.90 (s, 3 H, NCH_3); 8.30–8.70 (m, 12 H, CH_2). MS (*m/e*): M^+, 406 (100); 404 (100).

The third product was an oil. IR ($CHCl_3$): 1770, 1700 cm^{-1} (no Ph, NH or OH in IR). NMR ($CDCl_3$): τ 7.00 (s, NCH_3); 7.60–8.70 (m, CH_2). This was octahydro **1**, X=NMe as shown also by high resolution mass spectrometry. This reaction emphasizes the difficulty in avoiding inadvertent retrogression of the Diels–Alder adducts.

Catalytic reduction and hydrogenolysis of mono-adduct mixture at higher pressure

The same 2:1 mixture (155 mg) was reduced in EtOH (100 ml) using PtO_2 at 4 atm H_2 and room temp. After 24 hr removal of catalyst and solvent gave crude product (165 mg). Work up as above gave perhydro-isomers *anti*-**14** (11 mg) and *syn*-**15** (21 mg), again corresponding as above to the ratio of 2:1 but this is coincidental for here the third (oily) product, of similar spectral properties as described above was obtained in major amount (94 mg), in keeping with the lower stability of adducts in this case perhaps due to the higher pressure used and/or catalysis by HBr formed.

Isomer **14** had m.p. 115–117° (benzene). (Found: N, 7.79; M.W. 332.2067. $C_{19}H_{28}N_3O_3$ requires: N, 7.45%; M.W. 332.2099). IR ($CHCl_3$): 1780, 1710 cm^{-1}. NMR ($CDCl_3$): τ 6.05 (m, 1 H, CHO); 6.70 (m, 1 H, CHN); 6.95 (s, 3 H,

NCH_3); 7.70–8.80 (m, 22 H, CH_2). MS (*m/e*): M^+, 332 (9.7); 289 (14.5); 209 (11); 185 (23); 165 (100); 141 (50).

Isomer-**15** was an oil. (Found: N, 7.78; M.W. 332.2094). IR ($CHCl_3$): 1780, 1705 cm^{-1}. NMR ($CDCl_3$): τ 6.15 (m, 1 H, CHO); 6.75 (m, 1 H, CHN); 7.00 (s, 3 H NCH_3); 7.80–9.00 (m, 22 H, CH_2). MS (m/e): M^+, 332 (5); 289 (4); 209 (15); 166 (100); 138 (85).

The third product was an oil. IR ($CHCl_3$): 1780, 1720 cm^{-1}, no Ph, NH, OH in IR. NMR ($CDCl_3$): τ 7.00 (s, NCH_3); 7.60–9.00 (m, CH_2).

Attempted chemical reductions

(a) The *anti*-hexahydro **12**, Ar=*p*−Br C_6H_4 (30 mg) was dissolved in EtOH (10 ml) and was reduced in the presence of 2 drops conc NH_4OH and PtO_2 during 24 hr at room temp and 3 atm H_2 pressure. Removal of catalyst and solvent followed by ether extraction gave an oily amino-alcohol **16**, formed by hydrogenolysis of the N–O and C–Br bonds and reduction of the aromatic ring. (Found: M.W. 334.2291. $C_{19}H_{30}N_2O_3$ requires: 334.2256). IR ($CHCl_3$): 3620, 3360, 1780, 1720 cm^{-1}. NMR ($CDCl_3$): τ 6.20 (m, 1 H, CHO); 7.00 (s, 3 H, NCH_3); 7.70 (2 H, CHN); 7.80–9.30 (m, 20 H, CH_2). MS (*m/e*): M^+, 334 (5.5); 220 (17); 206 (16); 205 (100); 161 (39); 149 (74); 147 (45); 138 (24). (b) Reduction of the *anti*-mono-adduct **10** (60 mg) in EtOH (10 ml) as in part (a) also gave **16**. Heating the latter with Ac_2O–NaOAc at 100 for 3 hr and extraction with hexane afforded the oily diacetate. IR ($CHCl_3$): 1780, 1750, 1710, 1600, 1450, 1370, 1100 cm^{-1}. NMR ($CDCl_3$): τ 5.10 (m, 1 H, CHO); 5.60 (m, 2 H, CHN); 7.00 (s, 3 H, NCH_3); 7.40–9.30 (m, 29 H, CH_2); 8.10 (6 H, CH_3COO; CH_3CN). MS (*m/e*): M^+-COCH_3, 375 (6.3); 333 (13); 316 (19); 273 (33); 233 (13); 221 (9); 167 (25); 149 (100).

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