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Diels-Alder cycloadditions of 1,3-cyclohexadien-4,5-diones (*o*-benzoquinones) with norbornadiene. Part I. Synthesis.

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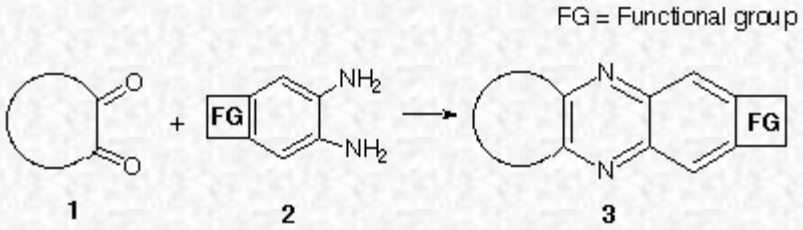
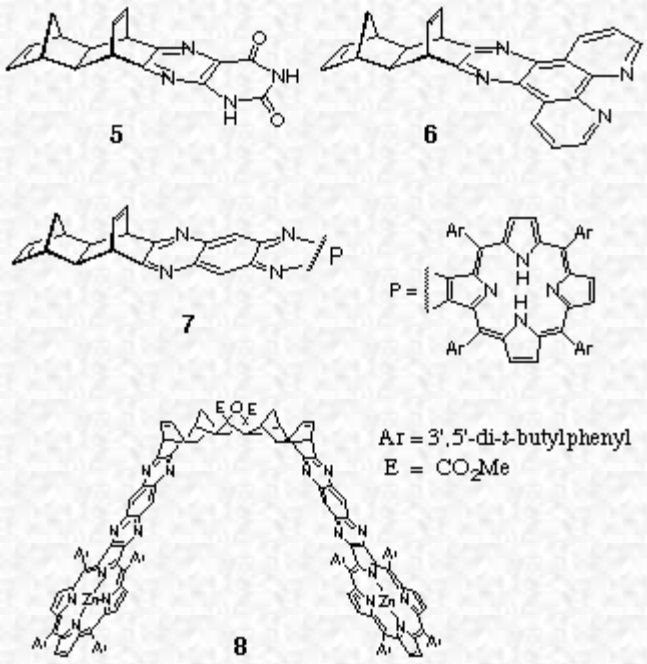
Abstract. Cycloadditions between *o*-chloranil and norbornadiene produced a range of geometrical variants which were characterised as quinoxaline derivatives. Two ether products were also observed resulting from hetero Diels-Alder reactions. Photochemical irradiation of **20** produced the cage compound **22** as a result of an internal (2+2)p cycloaddition.

Intoduction. In this paper we describe some syntheses of *o*-benzoquinone, *o*-chloranil and 2,5-di-(*t*-bu)-benzoquinone with norbornadiene.[1,2] The resulting alicyclic a-diones are used in our BLOCK assembly protocols [3] for Schiff's base condensations with substituted *o*-phenylene diamines **2** to yield quinoxalines **3** suitable as building BLOCKs (Scheme 1). VRID01SNYAE00 ÷ySONY HP CD-Writer+ 8200a1.0gú÷yarious effectors such as porphyrin **7** [4,5], uracil **5** [6] and the 1,10-phenantroline ligand **6** [7] have been attached to these BLOCKs which are then used to prepare large supramolecular systems such as bis-porphyrin host **8** (Scheme 2).



Scheme 1.



Scheme 2.

Cycloaddition of *o*-chloranil. The addition of *o*-chloranil (**10**) to norbornadiene (**9**) (Figure 1) has been previously utilised for the synthesis of the linear a-dione BLOCK (**11**).[2] However, a closer examination of the crude reaction has revealed the presence of all the possible geometries of addition with the four dione products (**11-14**) which were characterised as their phenylenediamine condensation products **18-21** (Figure 1) (due to their readiness to add water to form hydrates eg. **11a**). The hetero Diels-Alder adducts **15** and **16** are also observed from heteronuclear reaction between **10** and norbornadiene. Standard conditions for this condensation reaction are reflux in ethanol, however we have shown that the same reaction can also be carried out un! der high pressure (in DCM) in high yields. Furthermore, in a separate experiment, a sample of pure hydrate **11a** was condensed with phenylene diamine to produce **18** under similar high pressure conditions (DCM, overnight, 53% yield). In contrast, the reaction of parent *o*-benzoquinone with NBD (Figure 2) yields predominantly the linear *exo*- adduct **11**, with insignificant amounts of the other isomers.

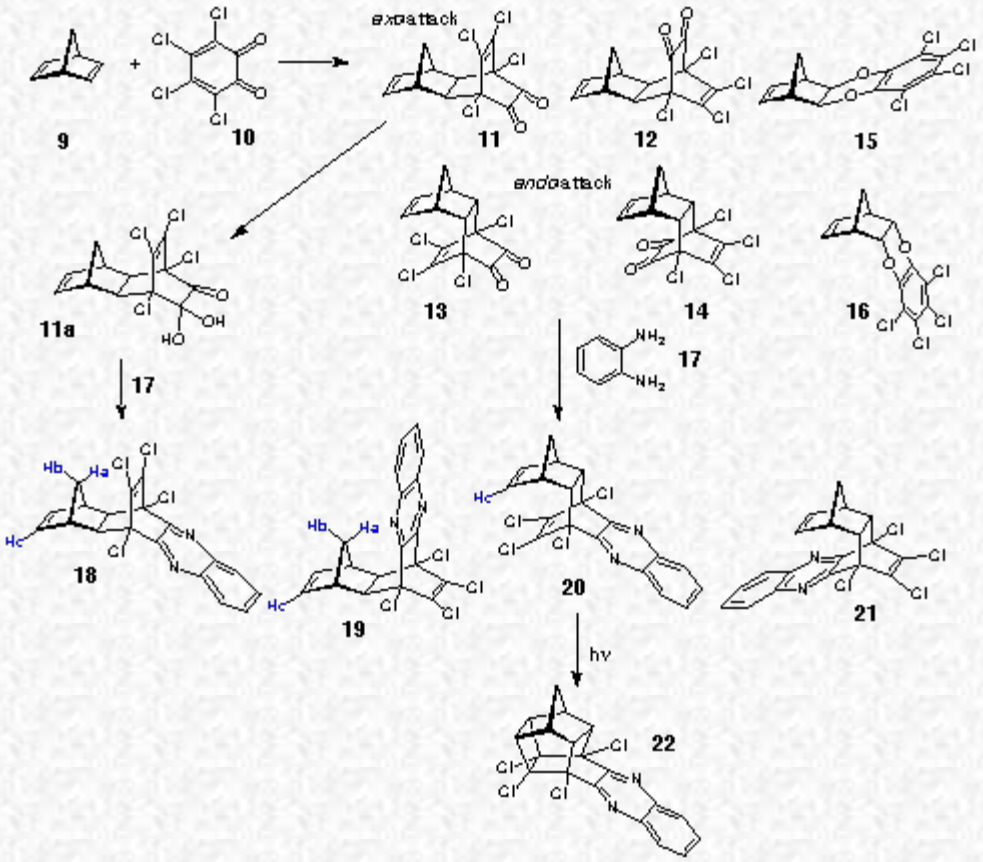


Figure 1. Cycloadditions between *o*-chloranil and norbornadiene.

In the case of *o*-chloranil and norbornadiene, a study was undertaken in order to establish the effects of temperature and solvent on the distribution of these adducts. The reaction of **9** and **10** was studied in benzene, chloroform and ethanol at several temperatures (ambient, 50 and 80 °C). The reaction solutions were immediately treated with *o*-phenylenediamine, ethanol added, and the mixture heated at reflux for 1 hour. After workup, the solutions were examined by HPLC (normal phase) to determine the isomer distribution. The retention times for each of the compounds was determined by partial column chromatographic separation (silica) of the various fractions coupled with ^{1}H-NMR spectra. The ether by-products were readily identifiable by their lack of proton resonances in the aromatic region and bicyclo[2.2.2] olefinic proton resonances, while the *endo*- addition pro! ducts were characterised by their characteristic chemical shifts and coupling patterns. For instance, in compound **18**, the methylene protons Ha and Hb reso nate at (d=2.00 and 2.42 respectively), whereas in **19** where these protons experience a large shielding by the proximal aromatic ring and resonate at d -0.67 and 0.85, respectively. There was no significant chemical shift of olefinic proton Hc in structure **20** as compared to compounds **18** and **19** (d=6.21, 6.33 and 6.19, respectively). In addition, the formation of the cage compound **22** from irradiation of quinoxaline **20** confirmed the assignment of the *endo*- addition products.

The results are summarised in Table 1 and reveal that the *exo*-linear adduct **18** is always the major addition product, followed by the *endo*-linear product **20**. The amount of products such as **20** and **21** increases as solvents other than ethanol are investigated explaining one possible reason why these compounds where not observed in earlier studies. The zero values shown in the table indicate that no amount of that isomer was observable using UV detection (254 nm).

An understanding of the isomer distribution shown in Figure 1 as gained from molecular modelling, along with the cycloaddition preferences of the parent *o*-benzoquinone and the 3,6-di-*tert*-butyl substituted *o*-benzoquinone, are presented in the subsequent paper. [8]

Table 1. Percentage isomer distribution for the cycloaddition between *o*-chloranil and norbornadiene[#]

	15	16	18	19	20	21
Benzene RT	3.7	0.3	90.6	0.25	5.0	0
50 °	6.3	1.2	82.8	0.37	8.2	1.2
80 °	5.6	0.95	84.5	0.4	8.2	0.3
$CHCl_3$ RT	4.6	0.8	84.8	0.7	7.5	0.2
50 °	3.6	0.5	88.3	1.4	6.2	0
80 °	3.6	0.3	90.2	0.5	5.4	0
EtOH RT	1.4	0.2	93.3	0.4	4.7	0
50 °	1.9	0.3	91.6	0.5	5.7	0
80 °	2.2	0.4	90.5	0.4	6.6	0

[#]R.T. reactions were stirred for 24 hours before quenching whereas heated reactions were stirred for 3 hours.

Cycloaddition of *o*-benzoquinone. Catechol **23** was oxidised by iodobenzene diacetate to produce *o*-benzoquinone **24** *in situ* [9] and this was trapped by norbornadiene **9** to form the molrac dione **25** as a stable orange solid in 60% yield, along with products **26-28** as observed minor components. Dione **25** is stable at room temperature and can be further reacted with dimethylacetylene dicarboxylate (DMAD) in the presence of ruthenium catalyst ($RuH_2CO(P(Ph)_3)_3$) [10] to form adduct **29** (Figure 2).

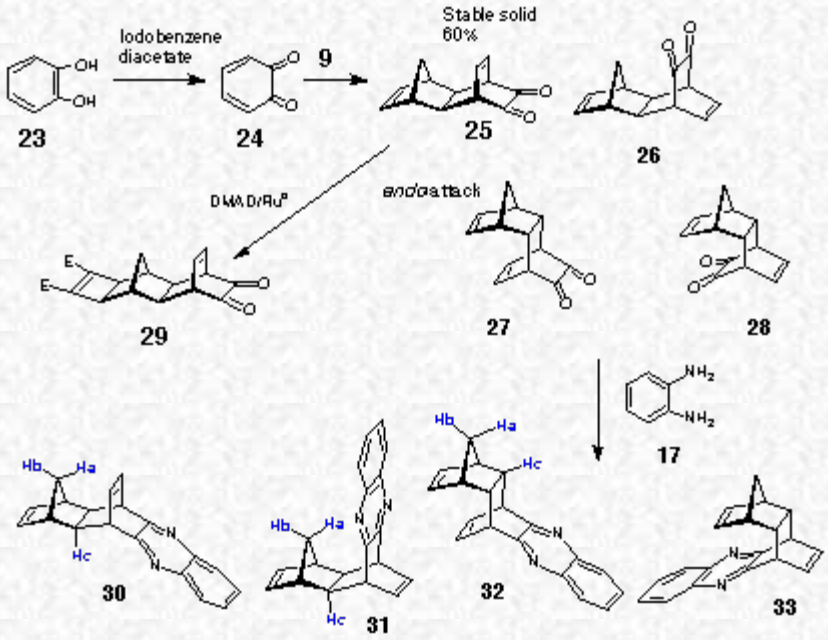


Figure 2. Synthesis of molrac diones **25** - **33**.

The formation of **25** as a major product occurs via a [4 + 2]p Diels-Alder cycloaddition. Similar to the *o*-chloranil reaction, attack can be either *endo*- or *exo*- to the norbornadiene ring and so there are four stereochemical dione products as well as two hetero-Diels Alder ether products possible. An examination of transition structure energetics has been employed in these Diels-Alder reactions in an attempt to understand product distributions. These results are presented in the subsequent paper [8]. The theoretical analysis reveals that dione **25** should be the dominant product, as observed by experiment.

The mixture of diones **25-28** was transformed to quinoxalines **30-33** as described above for the *o*-chloranil compounds **18-21**. The product stereochemistry was established on the basis of the characteristic ^{1}H-NMR chemical shifts. The chemical shifts of methylene protons Ha and Hb in adduct **30** occurs at d=1.18 and 2.76 while in adduct **31** these

proton are shielded by the aromatic ring and appear at d= -0.54 and 0.86, respectively. Furthermore, *endo*- protons Hc in the linear product **30** are more shielded (d=2.09), as compared to the product **31** (d=1.77)**.** *Endo*- product **32** methylene proton signals Ha and Hb are found at d=1.43 and 1.77, respectively, while the *exo* protons are found to be at d=2.60. Also the ! norb ornene olefinic protons are shifted to 6.7 ppm due to effects of the second double bond held in close proximity.

***t*-Butylbenzoquinone cycloadditions.** In an effort to obtain an alternative dione to *o*-chloranil to react with norbornadiene, the *tert*-butyl substituted benzoquinone (**38**) (Figure 3) was targeted for synthesis since similar molecules have been observed to undergo cycloaddition reactions.[11,12] This material should enhance the solubility of any cycloaddition products as well as leaving an olefin available for derivatisation in adducts such as **40**.

The synthesis of **38** was• p]›Æ“§>usÍ§dûi@™¹¡ú¡ :—à¢’VgÔa“$ZœÒV[m™¢J´¢¤è¢£Ã–ã š23«Á›¼æx~6¢•X{švw™? JuFZDÇÈ {Âh,y;®ØŠ)pùZ€È‡#˜gŸøoQ:9(–(ÚTç†iÿ‘~¡ù¢”H$ 7jù—‰ßÔˆ½ÄKJÊ¦e¦‘É^´˜X(zr˜¦>ŠoCªVkšŒ-Š‘vBÚ \ƒ[š2Æ›ÓwÖói¸¸ZÚBÔÈT”ÿ*3Ûù\{i€IÉ{æÖEÄ¸šlÚœªh‰2I£_ê–Ùhtšùné¸‰6øFyy¤c9‰éÂf²c£‰©‹wi*³ê °¦ª‹E$C ¢ŒÉŸIÄªDJ˜rYN¾š«º™X9Xé_âçt‘©”üv,Ðõ˜îµ§úóÕ'Ê*™¸v©3Ù*ûæFca8ò Ujzðân"åbè')šÌÊŽ“®äb,ez¦ ¤úê6"¹ —ü…]4özÑJ_ñÚ'êŸn¦ê)×'',LÉÇ‘8Ù{[¦ºªYb¡Íªtõu laZ¨øgŽ‹±ˆšT â®àÚ,¶E&’º±…“‘µ¶jmÂ ³Ív»1Æ®6…g(ÛY-÷`÷ iÄé ¥Ãu±Ô¬ö·©†×¤¦„´,—¤„Zµ¦ ›f~ßH´1ª¥Òê™¨¤›››´Z³d‹Š Ø¶« uë,w‹¨{K¬¨Ú8ýZtÇ§´`ë‡‹£(7µ*ú·s•¸lx²3WŒãê·¸ È ¥â˜³ëºž‹VQ+¸`Ð™WŸ‹Š›Ú“kr¢<Çmy L:ûŸàˆ¬þ c»ù³u8¨»þx§µ?8šc¥råÎJk'S2/wÊV'Jªv-c®$±7{=4C^Þš¬¬KV;›ºH• $*›œ6(‹™ålïwa÷w· ±ÛCH)ErÊ~ðƒ®‹µº,ÈÉ’ù9»è·|9È&½.I?Â“ Ð»N(oxu^;†ó›¯ºÛ?¾ùI–é‘Y4ˆ²šÁ¦ö´(˜Àf ´£:8o‡µ7ÚK©Á¼s³$·'üÂ0Ã2<Ã4\Ã6|Ã8œÃ:¼Ã<Ü„%4§šZ„ÖŸd;£‘ã¿Væ6å,@¼cC£Ä)GÄSF-Oœ#Å•ÅWœœãT[ŸÓÅ=œ.Q,Æc|ÆhœÆj¼ÆlÜÆnüÆpÇr<Çt,y]ZÇo;ÁxÌ1¼Ç|,³~ü?=È‹S0ZLÈÓHˆ|:ÏH½‹¬¾: ¤¶ìa.èREÿ9É´[Y’ŒÉ)V‹ÓÊÉ·¬,¬m¦¼ós8fÆ™ŠP¾÷FPŠƒ‡ì‰ðØ§Œ¥Êë«º3Ûª3ã2¶«c³ì”’dË¾{§¿Q}+Ì¿H~0å‡º¬@ZÌP rËñôËOzÈ\ZD¾ùôÃÙDŒÈ¬iQ1ºöÛ¾ÌAÅZmá<˜Î¸.ÆÈ—½uÁB—Äëì“ew¿{½Çy¶þìš ì²$<¤@åTCbuÔÜjd<ÿúÌ€¬6J£ \½\>uº'e|µxz² ã¦};Œèõ@ÞÏûºv‹y÷‘ø²ŠEzãÆµE¢ †Ê mÅ¦€ƒË|"ë¡ä,,“8‹ÁzÍ¬9ˆxÏ:E–ü“~Èkxºc¼aWZG4¿E7‹™»Çv:Õv §,ü¸ŽÊâÆÊÌ™Õ˜b~}tÄ§ZÔgýÛe~PýÈV}Ë{£µAÝÖ,cu\Æ5HÆ‹×*yƒ4Ù=J Ÿ´Ø_ƒÐÌ½vÝº$+ °áÚ~"ŒØ5Ë»5¥BŒMÙ¨Ëa5Ôçè´üÌÙÝU¾¼kçÂÜØ—¤}¨wÕ:j=´¬¸Ú²=Û´]Û¶}Û¸ÍÇaœÛ ¢•Ù¼ŽæüÛÊƒ¡Âí0ƒWÜÈ};GIF87a¢Z÷ÿÿÿ!ù,¢Z@ÿH°`A\È°¡Ã‡#JœH±¢Å‹3jÜÈ±£Ç 5*82¤É“(SZ,€%Ë– _Â $™P¦L•oæ$És§À’@q Ut¨Ñ£H3Ö<ÈôÎ‰OOÖDø3'ÕžX[^ê3©W‰E¿,58rêV±h¥rý5-R³mW6µz0îO»Ïjå¨w¯Û¿^ûæŠ °áËËÌ*ÜÇKA*®8¹±eÄ•¡^Þ¼9óXÎ CÓÝ(X´é¯žŸ^Íºµë×tKÃžM»¶íÛ¸sëÞÍÛ©ß«²{N¼¸ñãm"_ž¼+óçÐ £_T¾¶úÂÈ”_·žu¦N Á™‡¨åŒ}fwé¿7GO<°Ž0â—ðŸâV Ÿ¾"üð‰ß{§Â/ÜÓ‘>WòÆÕ<îÇFÝV’/ã‹çÊ(‡´åp? ÖbHsÍ¸v”sºêBw²a*œâ¹"ñüYÆ]Zì(ŠC/veÐ¤Í«_œ0qY&“FÏxìš”A&öØd—möÙ=äÔ¯6%x5_\{|&Õ†úU5_S$X€N‡¢€R| ™rë}öáˆk%1Q1eöóÌlòñu©e˜a[–9Ó";^¬¦1Ù¸ÍÃ¾¹m°Çî4Ø,+w]œ»k–t·nóê ßñâB™Š{çº{úúÒþÎzÚ<ûn|áwË>êò;'½ºòÐOÞ| ò³CO=öÏW¿}Íß{_ææ¤†_=M—Ÿ?üéç«dûdy¶þïoÃÿ¾Sä?œ¸õÛïÓÿ HÀð€L ÈÀÜ|K` Œ X¨¥- Zp,4™ßXA nÐÜßGHÂ¢, ; evidence of decomposition. The reaction mixture disolved in chloroform and passed through a short silica column eluting with chloroform to afford **18** (64 mg, 53 %, m.p. 190 °C).

Quinoxaline 18.

^{1}H NMR ($CDCl_3$): d 1.47 (1H, d of t, J_d=10.3 Hz, J_t=0.9 Hz); 2.02 (1H, d, J=10.3 Hz); 2.42 (2H, d, J=0.9 Hz); 3.29 (2H, t, J=1.8 Hz); 6.33 (2H, t, J=1.8 Hz); 7.80 (2H, m); 8.18 (2H, m); m.p. 190 °C.

Quinoxaline 19.

^{1}H NMR ($CDCl_3$): d -0.67 (1H, d, J=10.5 Hz); 0.85 (1H, dt, J_d=10.5 Hz, J_t=1.5 Hz); 2.87 (2H, d, J=1.3 Hz); 2.93 (2H, d, J=1.6 Hz); 6.1 (2H, m), 7.80 (2H, m); 8.18 (2H, m).

Quinoxaline 20.

^{1}H NMR ($CDCl_3$): d 1.54 (1H, d, J=8.8 Hz); 1.73 (1H, dt, J_d=8.8 Hz, J_t=1.7 Hz); 3.05 (2H, t, J=1.7 Hz); 3.26 (2H, d, t, J=1.7 Hz); 6.21 (2H, t, J=1.7 Hz); 7.80 (2H, m); 8.19 (2H, m).

‘Bird cage’ compound 22. The ‘bird cage" precursor **20** (37 mg, 0.09 mmol) was dissolved in $CDCl_3$ (400 ml) and irradiated at 300 nm for 50 minutes (Pyrex NMR tube). ^{1}H NMR revealed the loss of olefinic resonances and the

emergence of a methine signal. Solution was taken to dryness and material purified by column chromatography (silica) eluting with DCM / petroleum spirit (1:1) to give **22** as a pale solid, (m.p. 300 ^{o}C). Accurate mass: Found: 409.9727, calculated: 409.9727.

^{1}H NMR ($CDCl_3$): d 1.74 (1H, dt, J_d=12 Hz, J_t=1.8 Hz); 2.00 (1H, d, J=12 Hz); 2.92 (2H, d, J=1.8 Hz); 3.23 (2H, t, J=1.8 Hz); 3.50 (2H, q, J=1.8 Hz); 7.84 (2H, m); 8.29 (2H, m);

^{13}C: 36.7, 46.8, 50.9, 55.8, 77.4, 80.5, 129.5, 130.6, 142.2, 146.3.

Tetracyclo[6.2.2.1^{3,6}0^{2,7}]trideca-4,11-diene-9,10-dione 25. Catechol **23** (1.1 g, 10 mmol) along with **9** (160 ml) were dissolved in CH_3CN (720 ml) and PiDA (3.8 g, 12 mmol) added portionwise over 5 minutes. The solution was stirred under a N_2 atmosphere in the dark for 3 days. Whilst stirring continued, batchwise additions of **23** (1.1 g, 10 mmol) and PiDA (3.8 g, 12 mmol) were added every 2 days for 6 days to facilitate the production of larger amounts of **25**. The solvent was removed by rotary evaporation and the resulting solid was triturated with petroleum spirit. Combination and concentration of organic extracts produced a dark yellow solid that was purified by column chromatography (silica) eluting with $CHCl_3$. Recrystallised product from EtOAc/petroleum ether. (Yield 4.38 g, 55 %, m.p. 145 ^{o} C).

^{1}H NMR ($CDCl_3$): d 1.19 (1H, d, J = 9.1 Hz); 2.15 (2H, s); 2.57 (1H, d, J = 9.1 Hz); 2.97 (2H, t, J = 1.7 Hz); 3.53 (2H, t, J = 3.0 Hz); 6.30 (2H, t, J = 1.72Hz); 6.37 (2H, t, J = 3.0 Hz);

^{13}C NMR ($CDCl_3$): d 40.6; 43.2; 47.9; 51.9; 131.3; 140.7; 189.2.

Quinoxalines 30-33. Dione mixture (383 mg, 1.91 mmol) in ethanol/CH_3CN (1:1, 20 ml) along with phenylenediamine (280 mg, 2.1 mmol) was heated for 2 hours followed by stirring overnight at ambient temperature. Solution was taken to dryness under reduced pressure and purified by column chromatography (silica, eluting with CHCl3/petroleum ether 40%) followed by petroleum ether/ethyl acetate (20%) to give product.

Quinoxaline 30.

^{1}H NMR ($CDCl_3$): d 1.18 (1H, d, J=8.9 Hz); 2.09 (2H, s); 2.76 (1H, d, J=8.9 Hz); 2.84 (2H, s); 4.09 (2H, t, J=3.6 Hz); 6.19 (2H, s); 7.60-7.66 (2H, m); 7.90 - 7.96 (2H, m);

^{13}C NMR (CD_2Cl_2): d 42.8; 46.7; 46.9; 47.3; 129.1; 129.3; 130.1; 135.4; 140.7; 141.5.

Quinoxaline 31. (estimated from crude spectrum)

$_{1}$H NMR ($CDCl_3$): d -0.54 (1H, d); 0.86 (1H, d); 1.77 (2H, s); 2.69 (2H, s); 4.0 (2H, m); 5.7 (2H); 6.0 (2H, t, J=3.6 Hz); 7.62-7.65 (2H, m); 7.92-7.96 (2H, m).

Quinoxaline 32. (estimated from crude spectrum)

^{1}H NMR ($CDCl_3$): d 1.43 (1H, d); 1.77 (1H, d); 2.60 (2H, s); 2.93 (2H, s); 6.0 (2H, s); 6.7 (2H, m).

Dimethyl-pentacyclo[8.2.2.1^{3,8}0^{2,9}0^{4,7}]pentadeca-5,13-diene-11,12-dione-5,6-dicarboxylate 29. Dione **25** (1.0 g, 5 mmol), DMAD (20 ml) and $RuH_2CO(PPh_3)_3$ catalyst (246 mg, 0.27 mmol) were dissolved in C_6H_6 (40 ml) and heated under reflux under a N_2 atmosphere for 2 days. The solution was concentrated to dryness and purified by column chromatography (silica) eluting with $CHCl_3$. The product was recrystallised from EtOAc/petroleum ether and pumped under vacuum. (Yield 345 mg, 20%, m.p. 176 ^{o}C).

^{1}H NMR ($CDCl_3$): d 0.88 (1H, t, J = 7.2 Hz); 1.11 (1H, d, J = 12.1 Hz); 1.26 (2H, t, J = 7.2 Hz); 1.55 (2H, s); 2.06 (2H, m); 2.15 (1H, d, J = 12.1 Hz); 2.65 (2H, m); 3.78 (6H, m); 6.39 (2H, m).

^{13}C NMR ($CDCl_3$): d 27.8; 39.9; 40.9; 42.5; 47.9; 51.9; 53.4; 128.6; 130.8; 132.8; 141.1; 161.1; 187.1.

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one 35. Method by Paquette *et al*. [12] Tribromophenol (**34**) (50 g, 0.2 mol) was dissolved in MeOH (250 ml) and glacial acetic acid (250 ml) and cooled in an ice bath. Bromine (12 ml, 0.23 mol) was added dropwise with stirring. Upon completion of addition, H_2O (500 ml) was added and the precipitated material removed by filtration. The solids were dissolved in petroleum spirit, washed $Na_2S_2O_5$ solution (10%, 400 ml), $NaHCO_3$ solution and dried (Na_2SO_4). Solvent removal yielded **35** as a yellow solid (63.61 g. 98%, m.p. 77 ^oC, lit. 80 ^oC).

^1H NMR ($CDCl_3$): d 1.13 (9H, s); 1.24 (18H, s); 6.90 (2H, s);

^{13}C: 25.8, 26.4, 28.8, 29.4, 29.7, 34.9, 39.9, 72.5, 139.8,141.4, 145.2, 184.8.

4-Acetoxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one 36. Method by Paquette *et al*. [12] Bromomaterial **35** (10.24 g, 29 mmol) was dissolved in acetic acid (100 ml) along with NaOAc (17.3 g, 21 mmol) and the solution heated at 65 uC for around 20 hours. Water was added and the solution extracted with Et_2O (2 x 200 ml). Combined organic extracts were washed H_2O, $NaHCO_3$ solution (3 x 300 ml), H_2O and dried (Na_2SO_4). Solvent removal produced a yellow oil that solidified upon standing (8.5 g, 88%) which was used in the next step without further purification.

^1H NMR ($CDCl_3$): d 0.97 (9H, s), 1.23 (18H, s); 2.07 (3H, s); 6.47 (2H, s).

1-Acetoxy-2-hydroxy-3,6-di-*tert*-butylbenzene 37. Method by Paquette *et al*. [12] Acetate (**36**) (2 g, 6 mmol) was dissolved in benzene (1 l) and irradiated with 450W medium pressure mercury lamp through pyrex for 2 hours while N_2 was bubbled through the solution. The solvent was removed by rotary evaporation to give a yellow oil which was crystallised from diethyl ether/petroleum spirit to give **37** as a fluffy white solid (0.51 g, 31%, m.p 177 ^oC, lit. 176 ^oC).

^1H NMR ($CDCl_3$): d 1.34 (9H, s); 1.41 (9H, s); 2.41 (3H, s); 4.92 (bs, 1H); 6.75 (1H, d, J=9 Hz); 7.10 (1H, d, J=9 Hz).

3,6-Di-*tert*-butyl-*o*-benzoquinone 38. Method by Paquette *et al*. [12] $NaHCO_3$ (150 mg, 1.8 mmol) was added to a solution of MeOH (16 ml) and water (2 ml) along with $MnCl_2$ (5 mg). Acetate (**37**) (400 mg, 1.5 mmol) was added all at once and O_2 bubbled through the stirred solution for 50 minutes. MeOH was removed by rotary evaporation and the remaining solution extracted with CCl_4 (3 x 20 ml) with combined extracts dried (Na_2SO_4) and concentrated to give a dark green solid. (m.p 186 ^oC, lit. 200-204 ^oC). Material was used without further purification.

^1H NMR ($CDCl_3$): d 1.23 (18H, s); 6.67 (2H, s).

Hetero Diels-Alder adduct 39. *t*-Butyl benzoquinone **38** (250 mg, 1.1 mmol) was dissolved in benzene (20 ml) along with NBD (500 ml) and the solution was heated in a sealed tube at 80 &127;^oC for 1 day, 100 &127;^oC for 4 days, and 110 &127;^oC for 1 day until the reaction was judged to be complete (NMR). The solution was taken to dryness to give a yellow powder which was adsorbed onto silica and placed atop a column and eluted with petroleum spirit to give **39** (295 mg, 83%, m.p 169 ^oC). Uninterpretable mass spectrum.

^1H NMR ($CDCl_3$): d 1.39 (18H, s); 1.86 (1H, dt, J=2, 9.0 Hz); 2.62 (1H, d, J=9.0 Hz); 3.13 (2H, t, J=2.0 Hz); 3.97 (2H, 2, J=2.0 Hz); 6.17 (2H, t, J=3.0 Hz); 6.84 (2H, s);

^{13}C ($CDCl_3$): d 29.9, 34.2, 43.9, 47.4,79.2, 118.6, 136.6, 137.5, 147.9.

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