Diels−Alder Reactions of 5-Alkyl-1,3-cyclopentadienes

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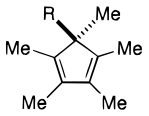
Received May 5, 1997[⊗]

Facial selectivity in the Diels−Alder reactions of 1,3-cyclopentadienes substituted at C-5 by a variety of simple alkyl groups has been assessed with a number of dienophiles. The results are consistent with an explanation based on steric hindrance. Syn addition is more favored with sterically less demanding dienophiles. Diene **6**, which is substituted at C-5 with methoxymethyl, shows a remarkable preference for syn addition with less encumbered dienophiles. This may indicate a conformational difference in its syn transition state relative to the transition states for addition syn to methyl, ethyl, or *n*-butyl substituents (dienes **1**, **4**, and **5**). Dienophiles are more reluctant to add syn to the larger C-5 group with 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (**2**) and derivatives (**3**, and **7**) and conformational effects become very important when C-5 bears two alkyl groups, as in dienes **3** and **7**.

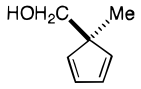
Introduction

Plane−nonsymmetrically disposed substituents on the diene or the dienophile are not infrequently used in synthesis as stereochemical control elements in Diels−Alder reactions, directing addition to the sterically less hindered face of the addend.[1] In this regard, alkyl groups are considered to present steric bulk without much complication from the stereoelectronic phenomena that have been proposed[2] to explain some apparently contrasteric facial selectivities associated with smaller heteroatom substituents. It is important from both the synthetic and theoretical points of view that facial selectivity with the smallest, archetypal alkyl-substituted dienes be mapped experimentally. In particular, our own *ab initio* computational examination of this type of facial selectivity has suggested that the simplest alkyl-substituted diene, 5-methyl-1,3-cyclopentadiene (**1**), should show little facial selectivity.[3] However, the experimental results with **1** in the literature are contradictory. McLean and Haynes[4] reported that there was no facial selectivity whatsoever in the reaction of **1** with *N*-phenylmaleimide, but Mironov[5] stated that, with maleic anhydride, the ratio of anti to syn addition was 12:1. (With other plane−nonsymmetric dienes, *N*-phenylmaleimide and maleic anhydride have shown negligible differences in facial selectivity.[6,7]) On the other hand, Ford[8] was able to detect only the product of addition syn to the methyl group of **1** when the dienophile was benzyne, and Adam and co-workers[9] indicated that syn addition was the predominant reaction between **1** and 4-methyl-1,2,4-triazoline-3,5-dione. *N*-Phenylmaleimide, maleic anhydride, and other ethylenic dienophiles all had very similar facial selectivities (about 80% anti addition) in their reactions with 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (**2**),[6] which offers the same facial alternatives as **1**, and Adam's group reported 75% anti addition for 4-methyl-1,2,4-triazoline-3,5-dione with **2**, in contrast with their result with **1**.[10] Adam also examined some reactions of other pentamethyl dienes including **3**.[10]

1 R = Me
4 R = Et
5 R = *n*-Bu
6 R = CH_2OMe
42 R = CH_2OBn



2 R = H
3 R = Et
7 R = CH_2OMe
41 R = Me
44 R = CH_2OH



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We have examined facial selectivities with a number of plane−nonsymmetric 5-alkyl-substituted cyclopentadiene derivatives (**1**−**7**), and the results are presented here.

Results and Discussion

Dienes **1**, **3**, **4**, **5**, and **7** were prepared by alkylation of lithium anions derived from cyclopentadiene or 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (**2**). Diene **6** was produced more cleanly via cyclopentadienylthallium. Dienes

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) For a very recent example with a plane−nonsymmetric diene, see: Skoda-Földes, R.; Jeges, G.; Kollár, L.; Horváth, J.; Tuba, Z. *J. Org. Chem.* **1997**, *62*, 1326−1332.

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(3) (a) Poirier, R. A.; Pye, C. C.; Xidos, J. D.; Burnell, D. J. *J. Org. Chem.* **1995**, *60*, 2328−2329. (b) Xidos, J. D.; Poirier, R. A.; Pye, C. C.; Burnell, D. J., manuscript submitted to *J. Org. Chem.*

(4) McLean S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2313−2327.

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(6) Burnell, D. J.; Valenta, Z. *J. Chem. Soc., Chem. Commun.* **1985**, 1247−1248. An earlier study reported a 3.5:1 ratio for the anti and syn adducts, respectively, with maleic anhydride: Mironov, V. A.; Fadeeva, T. M.; Pashegorova, V. S.; Stepanyants, A. U.; Akhrem, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 423−425.

(7) (a) Burnell, D. J.; Goodbrand, H. B.; Kaiser, S. M.; Valenta, Z. *Can. J. Chem.* **1987**, *65*, 154−165. (b) Burnell, D. J.; Valenta, Z. *Can. J. Chem.* **1991**, *69*, 179−184.

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(9) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007−3014.

(10) Adam, W.; Jacob, U.; Prein, M. *J. Chem. Soc., Chem. Commun.* **1995**, 839−840.

S0022-3263(97)00794-9 CCC: $14.00

Table 1. Relative Amounts (%) of the Anti Adducts from the Reactions of Dienes Monosubstituted at C-5

	dienophile		
diene	NPM	PTAD	TCNE
1	60 (**8a**)	21 (**14**)	100 (**20**)
2	82 (**23**)	75 (**25**)	97 (**29**)
4	69 (**10**)	30 (**16**)	100 (**21**)
5	74 (**12**)	34 (**18**)	100 (**22**)
6	15 (**45**)	16 (**47**)	100 (**49**)

Table 2. Relative Amounts (%) of the Anti Adducts from the Reactions of Dienes Doubly Substituted at C-5

	dienophile				
diene	NPM	NQ	PTAD	DMAD	TCNE
3	96 (**31**)	95 (**33**)	≥95 (**35**)	81 (**37**)	≥97 (**39**)
7	86 (**50**)	88 (**52**)	74 (**54**)	73 (**56**)	93 (**58**)

1, **4**, **5**, and **6** were not isolated, but were purified and reacted immediately with *N*-phenylmaleimide (NPM), 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), or tetracyanoethylene (TCNE) at *ca.* −20 °C without the complication of 1,5-sigmatropic rearrangement of the dienes. Dienes **3** and **7** were isolated in high yield. Diels−Alder reactions with **2**, **3**, and **7** were carried out with NPM, 1,4-naphthoquinone (NQ), PTAD, dimethyl acetylenedicarboxylate (DMAD), and TCNE at room temperature.

Adduct ratios were determined by careful integration of the ^{1}H NMR spectra of the crude product mixtures, and these ratios are given in Tables 1 and 2. In most instances, homogeneous samples of at least the major adducts were then isolated by chromatography or crystallization. The adducts derived from **2**, **3**, and **7** proved to be difficult to separate, so NMR data for their minor adducts had to be extracted from spectra of the adduct mixtures. Care was taken to ensure that adducts ratios reflected kinetically controlled reactions. This was done by extended heating of purified adducts, by heating adducts in the presence of other dienophiles, and by following some reactions (in $CDCl_3$) by ^{1}H NMR. Facile equilibration was noted only in the reaction of **3** with TCNE.

Our computational work[3] led us to the following rationalization of facial selectivity in the Diels−Alder reactions of 5-substituted 1,3-cyclopentadienes. The magnitude of the steric interaction is different as a dienophile approaches one face of the diene or the other. The addends deform to reduce the steric interaction, and at the transition state the difference in steric hindrance is reflected almost entirely in a difference in the energy of deformation of the diene moiety. Due to the geometry of the Diels−Alder transition state (Figure 1), the hydrogen on C-5 of the diene significantly hinders an incoming dienophile. Steric hindrance is less when addition is syn to substituents such as F, OH, and NH_2, which have longer bonds to C-5 of the diene. Indeed, even Cl, SH, and CH_3 substituents are not much different from H at C-5 in terms of their steric interaction with the dienophile. At some point the sheer size of larger substituents, even if they are held by longer bonds to the C-5 carbon, overwhelms hindrance due the C-5 hydrogen.

The Diels−Alder reactions of the alkyl-substituted dienes were examined with the above rationalization in mind. The Diels−Alder reaction of **1** with NPM gave only slightly more of adduct **8a** (anti) than **9a** (syn) (Table 1),

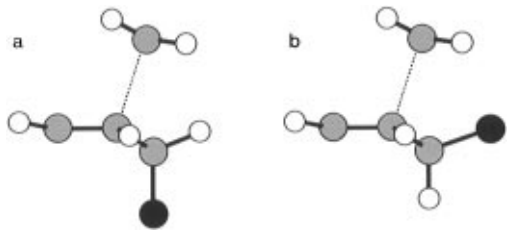
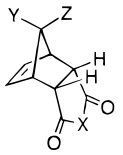


Figure 1. Side views (looking along the double bond of the dienophile) of transition states for the Diels−Alder reactions of a simple dienophile (ethylene) anti (a) and syn (b) to a substituent of about the same size as carbon on C-5 of 1,3-cyclopentadiene. Geometries are based on *ab initio* computational work.[3] The broken line represents an incipient σ-bond. In (a), the hydrogen on C-5 of cyclopentadiene is at a distance from the incoming dienophile that is similar to the dienophile−C-5 substituent distance in (b). However, differences in the shape and polarization of the C-5−H bond *versus* the C-5−substituent bond[3b] result in less steric hindrance in (b) than in (a).

consistent with our calculations[3] and the work of McLean and Haynes.[4] Unsubstituted maleimide gave adducts **8b**

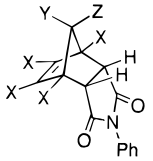


8a X = N–Ph, Y = Me, Z = H
8b X = N–H, Y = Me, Z = H
8c X = O, Y = Me, Z = H
9a X = N–Ph, Y = H, Z = Me
9b X = N–H, Y = H, Z = Me
9c X = O, Y = H, Z = Me

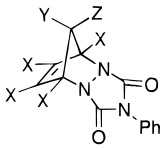
(anti) and **9b** (syn) in a 58:42 ratio, and addition of maleic anhydride gave **8c** (anti) and **9c** (syn), also in a ratio of 58:42, respectively. Lewis acid catalysis of the reaction of **1** with NPM, by the addition of 0.3 molar equiv of $SnCl_4$, gave **8a** (anti) and **9a** (syn) in a 63:37 ratio, an insignificant difference with the ratio from the uncatalyzed reaction. Increasing the length of the alkyl chain, as in dienes **4** and **5**, modestly enhanced the preponderance of the anti addition products, i.e., **10** (anti) and **12** (anti) > **11** (syn) and **13** (syn), respectively. This indicates that, with only a small energetic cost, these larger substituents can adopt conformations that are little different from a methyl group in terms of steric hindrance toward the incoming dienophile during syn addition. (In contrast, a tertiary butyl group at C-5 would not be able to avoid hindering an incoming dienophile, so it is not surprising that dimerization of such a diene would proceed exclusively by anti addition.[11])

PTAD is more reactive than NPM, but it is a sterically less demanding dienophile. Its reaction with **1** favored addition syn to the methyl group, i.e., **15** (syn) > **14** (anti). Increasing the chain length of the substituent modestly decreased the proportions of the syn adducts (**17** and **19**). Benzyne, like PTAD, should be less sterically demanding than NPM, and therefore it should no longer be surprising that syn addition was noted by Ford.[8] Similarly, acetylenic dienophiles should result in less steric hindrance with the 5-substituent on a diene. This is consistent with the modest preference for an apparently

(11) Hughes, R. P.; Kowalski, A. S.; Lomprey, J. R.; Neithamer, D. R. *J. Org. Chem.* **1996**, *61*, 401−404.



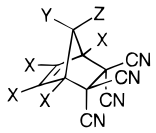
10	X = H,	Y = Et,	Z = H
11	X = H,	Y = H,	Z = Et
12	X = H,	Y = *n*-Bu,	Z = H
13	X = H,	Y = H,	Z = *n*-Bu
23	X = Me,	Y = Me,	Z = H
24	X = Me,	Y = H,	Z = Me
31	X = Me,	Y = Et,	Z = Me
32	X = Me,	Y = Me,	Z = Et
45	X = H,	Y = CH_2OMe,	Z = H
46	X = H,	Y = H,	Z = CH_2OMe
50	X = Me,	Y = CH_2OMe,	Z = Me
51	X = Me,	Y = Me,	Z = CH_2OMe



14	X = H,	Y = Me,	Z = H
15	X = H,	Y = H,	Z = Me
16	X = H,	Y = Et,	Z = H
17	X = H,	Y = H,	Z = Et
18	X = H,	Y = *n*-Bu,	Z = H
19	X = H,	Y = H,	Z = *n*-Bu
25	X = Me,	Y = Me,	Z = H
26	X = Me,	Y = H,	Z = Me
35	X = Me,	Y = Et,	Z = Me
36	X = Me,	Y = Me,	Z = Et
47	X = H,	Y = CH_2OMe,	Z = H
48	X = H,	Y = H,	Z = CH_2OMe
54	X = Me,	Y = CH_2OMe,	Z = Me
55	X = Me,	Y = Me,	Z = CH_2OMe

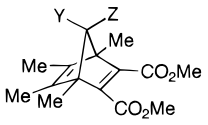
contrasteric syn addition of dimethyl acetylenedicarboxylate even to 9,10-dihydrofulvalene in an initial step of Paquette's dodecahedrane synthesis.[12] Halogen-substituted dienes had displayed an aversion to syn addition with PTAD[13] that was not seen with these alkyl-substituted dienes. This lends credence to our suggestion that syn addition of PTAD to the halogen dienes was hampered by a lone pair−lone pair interaction.[14] TCNE is also more reactive than NPM, but it is more sterically demanding. TCNE additions to **1**, **4**, and **5** proceeded in a facially specific manner, giving only the anti addition products **20**, **21**, and **22**. This paralleled the predominance for anti selectivity seen for TCNE with the halogen-substituted dienes.[13] The bulkier dienophile seems to increase steric hindrance with the H at C-5 (shorter bond) less than with a substituent (longer bond).

The facial selectivity with the pentamethyl diene **2** was greater than with **1**, **4**, or **5**. The reactions with NPM and PTAD gave mainly adducts **23** (anti) and **25** (anti), in the same proportions as in the literature, with PTAD being less reluctant to add syn to the methyl group.[6,10] With DMAD, the ratio of adduct **27** (anti) to **28** (syn) was 76:24, respectively, which was not significantly different from the ratio with PTAD. With TCNE the anti adduct **29** was the almost exclusive product. Thus, with all

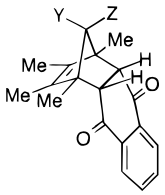


20	X = H,	Y = Me,	Z = H
21	X = H,	Y = Et,	Z = H
22	X = H,	Y = *n*-Bu,	Z = H
29	X = Me,	Y = Me,	Y = H
30	X = Me,	Y = H,	Y = Me
39	X = Me,	Y = Et,	Z = Me
40	X = Me,	Y = Me,	Z = Et
49	X = H,	Y = CH_2OMe,	Z = H
58	X = Me,	Y = CH_2OMe,	Z = Me
59	X = Me,	Y = Me,	Z = CH_2OMe

dienophiles **2** shows a reluctance for syn addition that can be overcome with **1** when a sterically less demanding dienophile is employed. Werstiuk and co-workers[15] have shown that stereoelectronic phenomena are unlikely to play a role in determining facial selectivity with **2**, so we propose that with **2**, unlike with **1**, the deformed diene moiety in the transition state for its syn addition suffers from a destabilization arising from coplanarity of the C-5 methyl with the methyls on C-1 and C-4.



27	Y = Me,	Z = H
28	Y = H,	Z = Me
37	Y = Et,	Z = Me
38	Y = Me,	Z = Et
56	Y = CH_2OMe,	Z = Me
57	Y = Me,	Z = CH_2OMe



33	Y = Et,	Z = Me
34	Y = Me,	Z = Et
52	Y = CH_2OMe,	Z = Me
53	Y = Me,	Z = CH_2OMe

Methyl and ethyl substituents had shown little difference in facial selectivity as C-5 substituents (**1** and **4**). However, when the methyl group was pitted against an ethyl, as in **3**, selectivity was very largely in favor of addition anti to ethyl, i.e., the major adducts with NPM, NQ, PTAD, DMAD, and TCNE were **31** (anti), **33** (anti), **35** (anti), **37** (anti), and **39** (anti).[16] (Indeed, in the reaction with PTAD the syn adduct **36** could not be detected.) These results were similar to those of Adam.[10] The C-5 methyl must force the ethyl group to adopt a conformation in which it would very effectively shield one face of the diene. The ethyl group had very little effect on the rate of addition syn to the methyl. A competitive reaction between **3** and **41** using NPM as the dienophile showed that **41** reacted about twice as fast as **3**, so the face of **3** bearing the C-5 methyl is as reactive as a face of **41**.[17]

We were curious why **1**, **4**, and **5** had only shown modest facial selectivity whereas in the literature only anti adducts had been reported for the methoxymethyl- and benzyloxymethyl-substituted dienes **6** and **42**.[18]

(12) (a) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5845−5855. (b) Paquette, L. A.; Weber, J. C.; Kobayashi, T.; Miyahara, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8591−8599.

(13) Wellman, M. A.; Burry, L. C.; Letourneau, J. E.; Bridson, J. N.; Miller, D. O.; Burnell, D. J. *J. Org. Chem.* **1997**, *62*, 939−946.

(14) Coxon, J. M.; Fong, S. T.; McDonald, D. Q.; Steel, P. J. *Tetrahedron Lett.* **1993,** *34*, 163−166.

(15) (a) Werstiuk, N. H.; Ma, J.; Macaulay, J. B.; Fallis, A. G. *Can. J. Chem.* **1992**, *70*, 2798−2808. (b) Werstiuk, N. H.; Ma, J. *Can. J. Chem.* **1994**, *72*, 2493−2505.

(16) "Syn" and "anti" addition is defined with dienes **3**, **7**, and **44** as relative to the ethyl, the methoxymethyl, or the hydroxymethyl on C-5.

(17) Diene **41** has twice as many reactive faces as **3**.

(18) (a) Corey, E. J.; Cheng, X.-M. *The Logic of Chemical Synthesis*; John Wiley & Sons: New York, 1989; pp 255−261 and references therein. (b) Tolbert, L. M.; Gregory, J. C.; Brock, C. P. *J. Org. Chem.* **1985**, *50*, 548−548.

Paquette[19] had pitted a hydroxymethyl versus methyl in diene **43**, but the facial selectivity was only modestly in favor of addition anti to the hydroxymethyl. This was attributed to small steric differences. The same facial alternatives were present in **44**, but both Adam[10] and Ishida[20] noted high facial selectivities, favoring addition anti to the hydroxymethyl. Thus, we decided to examine the Diels−Alder reactions of **6** (Table 1). NOE data for the major adducts (**46** and **48**) with NPM and PTAD showed that their vinyl hydrogens were near the hydrogen on the methano bridge. These were undoubtedly products of addition syn to the substituent, in contrast with the results reported for the Lewis acid-catalyzed reactions of **6** and the reactions of **42**,[18] and contrary to the expectation suggested by our data for dienes **1**, **4**, and **5**. Furthermore, reaction of **6** with the more sterically demanding TCNE behaved as expected: only the anti addition product **49** was obtained. For the moment, the selectivity that we have seen of **6** with NPM and PTAD defies unequivocal rationalization. We suspect that the explanation will involve a conformational effect that has hitherto been unimportant, because when methoxymethyl is pitted against methyl, as in diene **7**,[16] the facial selectivities are similar to those of **3** (Table 2), i.e., it is likely that the C-5 methyl forces the methoxymethyl group to adopt a conformation similar to that of the ethyl group in **3**.

In summary, facial selectivity with 5-alkyl-substituted 1,3-cyclopentadienes appears to be consistent with our computational model of control by steric hindrance. Conformational factors can influence the accessibility of a diene face, as in dienes **3** and **7**, and an unexpectedly high preference for syn addition to **6** was identified. With good data for alkyl-substituted dienes in hand, we will now be able to address the facial selectivity of these dienes computationally.

Experimental Section

General Methods. ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ solution unless otherwise noted; chemical shifts are relative to internal TMS. NOE data for adducts are provided as Supporting Information along with additional characterization data (IR, MS, HRMS, elemental analyses). ^{13}C NMR spectra are at 75 MHz in $CDCl_3$ unless otherwise noted; chemical shifts are relative to a solvent resonance. All reactions were performed under nitrogen. Representative procedures for the Diels−Alder reactions can be found below. The ratios of the adducts were obtained by careful integration of ^{1}H NMR spectra of the crude adduct mixtures. The conversion of dienes to adducts was very efficient in every case. Adducts were usually very similar in polarity, so flash chromatography (on silica gel with elution with hexane containing an increasing proportion of EtOAc) followed by recrystallization usually gave only small samples of adducts in homogeneous form.

5-Ethyl-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (3). To a solution of **2** (500 mg, 3.67 mmol) in THF (25 mL) at 0 °C was added dropwise *n*-butyllithium (1.7 mL of 2.5 M in hexane). The resulting slurry was stirred for 15 min before iodoethane (0.35 mL, 4.4 mmol) was added. The mixture was stirred at 0 °C for 3 h. The mixture was diluted with Et_2O, and the solution was washed thoroughly with H_2O and brine, dried ($MgSO_4$), and concentrated under vacuum to give **3** as a yellow oil (575 mg, 95%): ^{1}H NMR δ 1.76 (6H, s), 1.65 (6H, s), 1.41 (2H, q, J = 7.2 Hz), 0.85 (3H, s), 0.24 (3H, t, J = 7.2 Hz); ^{13}C NMR δ 139.6, 133.7, 56.1, 27.9, 21.9, 10.9, 9.6, 8.0.

5-(Methoxymethyl)-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (7). To a solution of **2** (500 mg, 3.67 mmol) in THF (25 mL) at 0 °C was added dropwise *n*-butyllithium (1.7 mL of 2.5 M in hexane). The resulting slurry was stirred for 10 min at rt before it was cooled to 0 °C, and chloromethoxymethane (295 mg, 3.66 mmol) was added dropwise. The mixture became clear, and it was stirred at 0 °C for 1 h. The mixture was diluted with Et_2O, and the solution was washed thoroughly with H_2O and brine, dried ($MgSO_4$), and concentrated under vacuum to give **7** as a yellow oil (520 mg, 86%): ^{1}H NMR δ 3.25 (2H, s), 3.24 (3H, s), 1.77 (6H, s), 1.75 (6H, s), 0.89 (3H, s); ^{13}C NMR δ 139.4, 133.9, 76.8,59.2, 56.6, 11.1, 10.1.

(3aα,4α,7α,7aα,8*r*)- (8a) and (3aα,4α,7α,7aα,8*s*)-3a,4,7,7a-Tetrahydro-8-methyl-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (9a). A representative procedure for Diels−Alder reactions with **1**, **4**, or **5** as the diene is given. *n*-Butyllithium (5.5 mmol) was added to a solution of 1,3-cyclopentadiene (0.40 mL, 5.0 mmol) in dry THF (15 mL) at 0 °C. After 10 min of stirring, the resulting cloudy solution was transferred over 20 min into a solution of iodomethane (1.5 mL, 24 mmol) in THF (10 mL) at −20 °C. The mixture was stirred for 1 h at −20 °C before it was transferred to a separatory funnel, quickly washed with cold brine (2 × 10 mL), and recooled to −20 °C. NPM (0.86 g, 5.0 mmol) was added, and the mixture was stirred for 3 h at −20 °C. The solution was washed with brine (2 × 10 mL), and evaporation of the solvent under vacuum gave a pale yellow solid (1.25 g). ^{1}H NMR analysis showed signals for two adducts in a 60:40 ratio. Flash column chromatography followed by recystallization from 5% CH_2Cl_2 in pentane provided homogeneous (by NMR) samples of **8a** (0.29 g, 23%) and **9a** (0.14 g, 11%). For anti adduct **8a**: colorless crystals; mp 129−130 °C; ^{1}H NMR δ 7.45−7.33 (3H, m), 7.14 (2H, br d, J = 7.0 Hz), 6.13 (2H, t, J = 1.9 Hz), 3.42 (2H, dd, J = 1.4, 2.9 Hz), 3.23 (2H, m), 2.22 (1H, q, J = 6.3 Hz), 0.91 (3H, d, J = 6.3 Hz); ^{13}C NMR δ 176.6, 134.7, 131.7, 128.9, 128.4, 126.5, 58.5, 50.5, 46.0, 11.6. Syn adduct **9a**: colorless crystals; mp 133−134.5 °C; ^{1}H NMR δ 7.47−7.34 (3H, m), 7.15 (2H, br d, J = 7.0 Hz), 6.30 (2H, t, J = 2.0 Hz), 3.48 (2H, dd, J = 1.6, 2.9 Hz), 3.18 (2H, m), 2.22 (1H, q, J = 6.8 Hz), 0.94 (3H, d, J = 6.8 Hz); ^{13}C NMR δ 177.4, 136.3, 131.9, 129.1, 128.5, 126.6, 59.1, 49.3, 44.0, 13.7.

(3aα,4α,7α,7aα,8*r*)- (8b) and (3aα,4α,7α,7aα,8*s*)-3a,4,7,7a-Tetrahydro-8-methyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (9b). Anti adduct **8b**: ^{1}H NMR δ 6.08 (2H, narrow m), 3.32 (2H, dd, J = 1.5, 2.9 Hz), 3.12 (2H, m), 2.14 (1H, q, J = 6.4 Hz), 0.89 (3H, d, J = 6.4 Hz); ^{13}C NMR δ 177.8, 131.7, 58.7, 50.0, 47.7, 11.8. Syn adduct **9b** (from mixture): ^{1}H NMR δ 6.24 (2H, br t, J = 2.0 Hz), 3.39 (2H, m), 3.04 (2H, m), 2.14 (1H, overlapped), 0.87 (3H, overlapped).

(3aα,4α,7α,7aα,8*r*)- (8c) and (3aα,4α,7α,7aα,8*s*)-3a,4,7,7a-Tetrahydro-8-methyl-4,7-methanoisobenzofuran-1,3-dione (9c). Anti adduct **8c** (from mixture): ^{1}H NMR δ 6.19 (2H, narrow m), 3.60 (2H, m), 3.23 (2H, m), 2.20 (1H, q, J = 6.3 Hz), 0.894 (3H, d, J = 6.3 Hz). Syn adduct **9c** (from mixture): ^{1}H NMR δ 6.34 (2H, t, J = 2.0 Hz), 3.62 (2H, m), 3.16 (2H, m), 2.25 (1H, q, J = 6.9 Hz), 0.886 (3H, d, J = 6.6 Hz).

(3aα,4α,7α,7aα,8*r*)- (10) and (3aα,4α,7α,7aα,8*s*)-8-Ethyl-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (11). Anti adduct **10**: colorless solid; mp 144−145 °C; ^{1}H NMR δ 7.46−7.35 (3H, m), 7.13 (2H, br d, J = 7.0 Hz), 6.13 (2H, t, J = 1.7 Hz), 3.42 (2H, dd, J = 1.6, 3.0 Hz), 3.34 (2H, m), 2.00 (1H, t, J = 7.2 Hz), 1.34 (2H, quintet, $J \approx$ 7.4 Hz), 0.83 (3H, t, J = 7.5 Hz); ^{13}C NMR δ 176.7, 134.1, 131.8, 129.0, 128.5, 126.5, 66.4, 48.6, 45.9, 19.1, 12.9. Syn adduct **11**: colorless solid; mp 124.5−125 °C; ^{1}H NMR δ 7.46−7.36 (3H, m), 7.15 (2H, br d, J = 7.0 Hz), 6.31 (2H, t, J = 1.9 Hz), 3.42 (2H, dd, J = 1.6, 2.7 Hz), 3.28 (2H, m), 2.02 (1H, t, J = 7.6 Hz), 1.26 (2H, quintet, $J \approx$ 7.4 Hz), 0.91 (3H, t, J = 7.4 Hz); ^{13}C NMR δ 177.3, 136.1, 131.9, 129.0, 128.5, 126.6, 66.9, 47.4, 44.1, 21.2, 11.9.

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(21) Atomic coordinates for the X−ray structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

(3aα,4α,7α,7aα,8*r*)- (12) and (3aα,4α,7α,7aα,8*s*)-8-*n*-Butyl-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (13). Anti adduct **12**: colorless solid; mp 145−146 °C; ^{1}H NMR δ 7.45−7.35 (3H, m), 7.13 (2H, br d, *J* = 8.6 Hz), 6.13 (2H, t, *J* = 1.7 Hz), 3.42 (2H, dd, *J* = 1.6, 2.9 Hz), 3.33 (2H, m), 2.07 (1H, t, *J* = 7.0 Hz), 1.28 (6H, m), 0.87 (3H, t, *J* = 7.1 Hz); ^{13}C NMR δ 176.8, 131.9, 129.0, 128.5, 126.6, 64.7, 48.9, 45.9, 30.0, 25.8, 22.7, 14.0. Syn adduct **13**: colorless solid; mp 82−84 °C; ^{1}H NMR δ 7.45−7.36 (3H, m), 7.14 (2H, br d, *J* = 7.1 Hz), 6.31 (2H, t, *J* = 2.0 Hz), 3.43 (2H, dd, *J* = 1.6, 2.8 Hz), 3.25 (2H, m), 2.07 (1H, t, *J* = 6.8 Hz), 1.26 (6H, m), 0.91 (3H, t, *J* = 6.9 Hz); ^{13}C NMR δ 177.4, 136.1, 131.9, 129.1, 128.6, 126.6, 65.2, 47.8, 44.3, 29.8, 27.9, 22.7, 14.0.

(10*r*)- (14) and (10*s*)-5,8-Dihydro-10-methyl-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (15). Anti adduct **14**: colorless solid; mp 126−127.5 °C; ^{1}H NMR δ 7.48−7.32 (5H, m), 6.37 (2H, t, *J* = 1.8 Hz), 4.86 (2H, dd, *J* = 1.7, 3.2 Hz), 2.86 (1H, q, *J* = 6.5 Hz), 0.96 (3H, d, *J* = 6.5 Hz); ^{13}C NMR δ 158.6, 135.4, 131.2, 129.1, 128.3, 125.5, 68.9, 54.0, 10.9. Syn adduct **15**: colorless solid; mp 140−141 °C; ^{1}H NMR δ 7.47−7.33 (5H, m), 6.47 (2H, t, *J* = 1.9 Hz), 4.77 (2H, dd, *J* = 1.5, 3.1 Hz), 2.36 (1H, q, *J* = 6.5 Hz), 1.21 (3H, d, *J* = 6.5 Hz); ^{13}C NMR δ 159.1, 132.9, 131.4, 129.1, 128.3, 125.5, 68.3, 55.9, 12.8.

(10*r*)- (16) and (10*s*)-10-Ethyl-5,8-dihydro-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (17). Anti adduct **16**: colorless solid; mp 105−106 °C; ^{1}H NMR δ 7.46−7.32 (5H, m), 6.35 (2H, t, *J* = 1.6 Hz), 4.92 (2H, dd, *J* = 1.6, 3.2 Hz), 2.68 (1H, t, *J* = 7.6 Hz), 1.30 (2H, m), 0.89 (3H, t, *J* = 7.4 Hz); ^{13}C NMR δ 158.5, 131.1, 129.2, 129.0, 128.2, 125.4, 67.4, 61.3, 18.7, 12.2. Syn adduct **17**: colorless solid; mp 108.5−109 °C; ^{1}H NMR δ 7.44−7.32 (5H, m), 6.44 (2H, t, *J* = 1.9 Hz), 4.82 (2H, dd, *J* = 1.5, 3.1 Hz), 2.11 (1H, t, *J* = 7.2 Hz), 1.57 (2H, m), 0.95 (3H, t, *J* = 7.3 Hz); ^{13}C NMR δ 158.7, 132.4, 131.1, 128.8, 128.0, 125.2, 66.3, 63.0, 20.0, 11.5.

(10*r*)- (18) and (10*s*)-10-*n*-Butyl-5,8-dihydro-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (19). Anti adduct **18**: colorless solid; mp 74−75 °C; ^{1}H NMR δ 7.46−7.34 (5H, m), 6.36 (2H, m), 4.92 (2H, dd, *J* = 1.8, 3.5 Hz), 2.75 (1H, m), 1.27 (6H, m), 0.89 (3H, t, *J* = 7.0 Hz); ^{13}C NMR δ 158.6, 131.2, 129.2, 129.1, 128.3, 125.4, 67.8, 59.8, 30.1, 25.3, 22.5, 13.8. Syn adduct **19**: colorless solid; mp 85.5−86 °C; ^{1}H NMR δ 7.46−7.35 (5H, m), 6.48 (2H, t, *J* = 1.9 Hz), 4.85 (2H, dd, *J* = 1.8, 3.3 Hz), 2.21 (1H, t, *J* = 7.1 Hz), 1.59 (2H, m), 1.35 (4H, m), 0.93 (3H, t, *J* = 6.8 Hz); ^{13}C NMR δ 159.0, 132.6, 131.3, 129.0, 128.3, 125.5, 66.8, 61.7, 29.5, 26.8, 22.5, 13.9.

(7*r*)-2,2,3,3-Tetracyano-7-methylbicyclo[2.2.1]hept-5-ene (20). Anti adduct **20**: colorless crystals; mp 193−194 °C; ^{1}H NMR (CD_3COCD_3) δ 6.67 (2H, t, *J* = 1.9 Hz), 4.16 (2H, dd, *J* = 1.6, 3.3 Hz), 2.80 (1H, m), 1.12 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (CD_3COCD_3) δ 136.8, 114.3, 113.3, 61.5, 54.8, 11.9.

(7*r*)-2,2,3,3-Tetracyano-7-ethylbicyclo[2.2.1]hept-5-ene (21). Anti adduct **21**: colorless crystals; mp 175.5−176 °C; ^{1}H NMR (CD_3COCD_3) δ 6.68 (2H, t, *J* = 1.9 Hz), 4.25 (2H, s), 2.55 (1H, t, *J* = 6.9 Hz), 2.05 (2H, quintet, *J* = 7.3 Hz), 0.96 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (CD_3COCD_3) δ 136.8, 114.2, 113.3, 62.0, 60.0, 20.2, 13.3.

(7*r*)-7-*n*-Butyl-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-ene (22). Anti adduct **22**: colorless crystals; mp 131−132.5 °C; ^{1}H NMR (CD_3COCD_3) δ 6.68 (2H, m), 4.24 (2H, dd, *J* = 1.5, 3.2 Hz), 2.61 (1H, t, *J* = 6.9 Hz), 1.50 (2H, m), 1.32 (4H, m), 0.89 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (CD_3COCD_3) δ 136.4, 113.8, 112.8, 59.8, 59.7, 47.9, 31.0, 26.0, 23.1, 14.2.

(3aα,4α,7α,7aα,8*r*)- (23) and (3aα,4α,7α,7aα,8*s*)-3a,4,7,7a-Tetrahydro-4,5,6,7,8-pentamethyl-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (24). A representative procedure for Diels−Alder reactions with **2**, **3**, or **7** as the diene. To a solution of **2** (250 mg, 1.84 mmol) in diethyl ether (15 mL) was added NPM (317 mg, 1.84 mmol), and the mixture was stirred for 16 h at rt. Evaporation of the solvent under vacuum left a yellow solid (365 mg). ^{1}H NMR analysis showed signals for two adducts in a 82:18 ratio. Flash column chromatography provided only a small homogeneous (by NMR) sample of **23** (44 mg). The bulk of the adduct was recovered as a mixture of **23** and **24**. For anti adduct **23**: colorless crystals; mp 136−137 °C; ^{1}H NMR δ 7.38 (3H, m), 7.06 (2H, m), 3.04 (2H, s), 1.60 (1H, q, *J* = 6.7 Hz), 1.59 (6H, s), 1.38 (6H, s), 0.64 (3H, d, *J* = 6.7 Hz); ^{13}C NMR δ 176.5, 133.6, 132.0, 129.1, 128.3, 126.6, 65.4, 58.1, 53.1, 14.7, 11.3, 7.5. Syn adduct **24** (from mixture): ^{1}H NMR (C_6D_6) δ 7.44 (2H, m), 7.00 (2H, m), 6.88 (1H, m), 3.04 (2H, s), 1.57 (6H, s), 1.56 (6H, s), 0.94 (1H, q, *J* = 6.5 Hz), 0.76 (3H, d, *J* = 6.5 Hz); ^{13}C NMR δ 177.0, 134.2, 132.0, 129.0, 128.3, 126.6, 65.9, 57.2, 51.2, 14.1, 11.1, 9.5.

(10*s*)- (25) and (10*r*)-5,8-Dihydro-5,6,7,8,10-pentamethyl-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (26). Anti adduct **25** (from mixture): ^{1}H NMR (C_6D_6) δ 7.43 (2H, m), 6.99 (2H. m), 6.87 (1H, m), 1.82 (1H, q, *J* = 6.6 Hz), 1.59 (6H, s), 1.50 (6H, s), 0.21 (3H, d, *J* = 6.6 Hz); ^{13}C NMR δ 159.2, 135.3, 131.6, 128.9, 128.1, 125.5, 79.8, 60.3, 13.2, 11.2, 8.0. Syn adduct **26** (from mixture): ^{1}H NMR (C_6D_6) δ 7.43 (2H, m), 6.99 (2H, m), 6.87 (1H, m), 1.57 (1H, q, *J* = 6.5 Hz), 1.56 (6H, s), 1.55 (6H, s), 0.75 (3H, d, *J* = 6.5 Hz); ^{13}C NMR δ 159.2, 135.3, 131.4, 128.9, 128.1, 125.3, 78.7, 60.3, 13.2, 11.2, 8.0.

(7*s*)- (27) and (7*r*)-2,3-Dicarbomethoxy-7-ethyl-1,4,5,6,7-pentamethylbicyclo[2.2.1]hepta-2,5-diene (28). Anti adduct **27** (from mixture): ^{1}H NMR δ 3.74 (6H, s), 2.35 (1H, q, *J* = 6.4 Hz), 1.64 (6H, s), 1.27 (6H, s), 0.71 (3H, d, *J* = 6.4 Hz); ^{13}C NMR δ 166.4, 155.7, 140.9, 80.6, 63.0, 51.6, 11.7, 11.2, 9.9. Syn adduct **28** (from mixture): ^{1}H NMR δ 3.75 (6H, s), 2.14 (1H, q, *J* = 6.4 Hz), 1.64 (6H, s), 1.27 (6H, s), 0.85 (3H, d, *J* = 6.4 Hz).

(7*s*)- (29) and (7*r*)-2,2,3,3-Tetracyano-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene (30). Anti adduct **29**: colorless needles; mp 170−171 °C; ^{1}H NMR δ 2.11 (1H, q, *J* = 6.3 Hz), 1.83 (6H, s), 1.54 (6H, s), 0.81 (3H, d, *J* = 6.3 Hz); ^{13}C NMR δ 137.9, 111.5, 110.8, 66.7, 57.5, 52.3, 12.1, 11.7, 8.3. Syn adduct **30** (only these signals discernable from mixture): ^{1}H NMR δ 1.61 (6H, s), 0.98 (3H, d, *J* = 6.1 Hz).

(3aα,4α,7α,7aα,8*r*)- (31) and (3aα,4α,7α,7aα,8*s*)-8-Ethyl-3a,4,7,7a-tetrahydro-4,5,6,7,8-pentamethyl-2-phenyl-4,7-methano-1,3(2*H*)-isoindole-1,3-dione (32). Anti adduct **31**: white solid; mp 105−106 °C; ^{1}H NMR δ 7.37 (3H, m), 7.06 (2H, m), 3.06 (2H, s), 1.62 (6H, s), 1.32 (6H, s), 1.28 (2H, q, *J* = 7.7 Hz), 0.82 (3H, s), 0.81 (3H, t, *J* = 7.7 Hz); ^{13}C NMR δ 177.1, 135.1, 132.1, 129.0, 128.3, 126.6, 66.9, 60.7, 51.5, 24.0, 14.1, 12.6, 11.5, 10.1. Syn adduct **32** (from mixture): ^{1}H NMR δ 7.37 (3H, m), 7.06 (2H, m), 3.13 (2H, s), 1.58 (6H, s), 1.27 (6H, s), 1.21 (2H, q, *J* = 6.4 Hz), 0.83 (3H, t, *J* = 6.4 Hz), 0.70 (3H, s).

(1α,4α,4aα,9aα,11*r*)- (33) and (1α,4α,4aα,9aα,11*s*)-11-Ethyl-1,4,4a,9a-tetrahydro-1,2,3,4,11-pentamethyl-1,4-methanoanthracene-9,10-dione (34). Anti adduct **33**: white solid; mp 132−133 °C; ^{1}H NMR (C_6D_6) δ 7.96 (2H, m), 7.00 (2H, m), 2.83 (2H, s), 1.25 (6H, s), 1.06 (2H, q, *J* = 7.7 Hz), 1.02 (6H, s), 0.65 (3H, t, *J* = 7.7 Hz), 0.46 (3H, s); ^{13}C NMR (C_6D_6) δ 197.5, 137.4, 135.8, 133.4, 126.2, 64.7, 63.0, 55.9, 24.1, 14.5, 12.3, 11.8, 11.0. Syn adduct **34** (from mixture): ^{1}H NMR (C_6D_6) δ 7.96 (2H, m), 7.00 (2H, m), 3.24 (2H, s), 1.19 (6H, s), 1.05 (2H, q, *J* = 7.1 Hz), 0.76 (3H, t, *J* = 7.1 Hz), 0.50 (6H, s), 0.46 (3H, s).

(10*r*)-10-Ethyl-5,8-dihydro-5,6,7,8,10-pentamethyl-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (35). Anti adduct **35**: colorless solid; mp 114−115 °C; ^{1}H NMR δ 7.34 (5H, m), 1.76 (6H, s), 1.68 (6H, s), 1.19 (2H, q, *J* = 7.6 Hz), 1.07 (3H, s), 0.85 (3H, t, *J* = 7.6 Hz); ^{13}C NMR δ 159.3, 132.4, 131.5, 128.9, 127.9, 125.3, 82.3, 62.3, 24.1, 13.9, 11.3, 11.2, 9.7. The structure was determined by X−ray crystallography.[21]

(7*r*)- (37) and (7*s*)-2,3-Dicarbomethoxy-7-ethyl-1,4,5,6,7-pentamethylbicyclo[2.2.1]hepta-2,5-diene (38). Anti adduct **37**: colorless oil. ^{1}H NMR δ 3.73 (6H, s), 1.66 (6H, s), 1.45 (2H, q, *J* = 7.7 Hz), 1.21 (6H, s), 1.00 (3H, s), 0.82 (3H, t, *J* = 7.7 Hz); ^{13}C NMR δ 166.7, 153.5, 142.6, 84.5, 67.1, 51.6, 25.7, 15.1, 11.9, 10.6, 9.4. Syn adduct **38** (from mixture): ^{1}H NMR δ 1.82 (6H, s), 1.79 (2H, q, *J* = 7.3 Hz), 1.53 (6H, s), 1.05 (3H, t, *J* = 7.3 Hz), 0.85 (3H, s).

(7*r*)- (39) and (7*s*)-2,2,3,3-Tetracyano-7-ethyl-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene (40). To a solution of diene **3** in ether was added an equimolar amount of TCNE

in one portion. After only 5 min of stirring at rt, the ratio of **39** to **40** was 97:3. After 24 h at rt the ratio was 9:1, and after the mixture was boiled for a further 20 h the ratio was 1:1. Anti adduct **39** (from mixture): ^{1}H NMR δ 1.86 (6H, s), 1.52 (6H, s), 1.31 (2H, q, J = 7.7 Hz), 1.28 (3H, s), 0.86 (3H, t, J = 7.7 Hz); ^{13}C NMR δ 141.1, 111.6, 111.1, 69.3, 64.5, 50.8, 27.0, 16.0, 12.2, 10.7, 9.6. Syn adduct **40** (from mixture): ^{1}H NMR δ 1.82 (6H, s), 1.79 (2H, q, J = 7.3 Hz), 1.53 (6H, s), 1.05 (3H, t, J = 7.3 Hz), 0.85 (3H, s); ^{13}C NMR δ 141.5, 111.6, 111.1, 69.2, 64.9, 50.6, 26.1, 16.4, 12.2, 10.8, 9.1.

(3aα,4α,7α,7aα,8*r*)- (45) and (3aα,4α,7α,7aα,8*s*)-3a,4,7,7a-Tetrahydro-8-methoxymethyl-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (46). A representative procedure for Diels−Alder reactions with **6** as the diene. Chloromethoxymethane (0.42 mL, 5.6 mmol) was added to a suspension of cyclopentadienylthallium (0.75 g, 2.8 mmol) in THF (15 mL) at −20 °C. The mixture was stirred at −20 °C for 5 h before it was quickly passed through a plug of glass wool into a solution of NPM (0.48 g, 2.8 mmol) in diethyl ether (5.0 mL) at −20 °C. The reaction mixture was stirred at −20 °C for 10 h before it was allowed to warm to rt. Evaporation of the solvent under vacuum provided a yellow solid. ^{1}H NMR analysis showed signals for two adducts in a 85:15 ratio. Flash column chromatography provided small, but homogeneous (by NMR), samples of **45** (0.065 g, 9%) and **46** (0.20 g, 25%). For anti adduct **45**: colorless crystals; mp 118.5−119 °C; ^{1}H NMR (C_6D_6) δ 7.33−7.13 (5H, m), 5.78 (2H, t, J = 1.7 Hz), 3.07 (2H, m), 2.96 (3H, s), 2.85 (2H, d, J = 7.0 Hz), 2.65 (2H, dd, J = 1.2, 2.8 Hz), 1.80 (1H, t, J = 7.0 Hz); ^{13}C NMR (C_6D_6) δ 175.8, 132.4, 129.2, 128.7, 128.4, 127.2, 69.9, 64.0, 58.9, 47.7, 46.1. Syn adduct **46**: colorless crystals; mp 113.5−114 °C; ^{1}H NMR (C_6D_6) δ 7.37−7.14 (5H, m), 5.94 (2H, t, J = 1.9 Hz), 3.01 (2H, m), 2.98 (3H, s), 2.66 (2H, dd, J = 1.3, 2.8 Hz), 2.59 (2H, d, J = 7.4 Hz), 2.04 (1H, t, J = 7.4 Hz); ^{13}C NMR δ 176.2, 136.3, 133.6, 129.2, 128.7, 127.2, 70.9, 63.9, 59.1, 46.8, 44.6.

(10*r*)- (47) and (10*s*)-5,8-Dihydro-10-(methoxymethyl)-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (48). Anti adduct **47** (from mixture): ^{1}H NMR δ 7.47−7.36 (5H, m), 6.38 (2H, t, J = 1.8 Hz), 5.01 (2H, dd, J = 1.8, 3.6 Hz), 3.30 (3H, s), 3.25 (2H, d, J = 7.0 Hz), 2.50 (1H, t, J = 6.9 Hz). Syn adduct **48**: white solid; mp 150−151.5 °C; ^{1}H NMR δ 7.47−7.36 (5H, m), 6.49 (2H, t, J = 1.9 Hz), 4.98 (2H, dd, J = 1.5, 3.3 Hz), 3.52 (2H, d, J = 6.7 Hz), 3.38 (3H, s), 2.51 (1H, t, J = 6.6 Hz); ^{13}C NMR δ 158.7, 132.3, 131.2, 129.1, 128.4, 125.5, 69.2, 65.6, 60.4, 59.2.

(7*r*)-2,2,3,3-Tetracyano-7-(methoxymethyl)bicyclo-[2.2.1]hept-5-ene (49). Anti adduct **49**: colorless crystals; mp 143−144 °C; ^{1}H NMR δ 6.61 (2H, m), 3.92 (2H, dd, J = 1.7, 3.4 Hz), 3.34 (2H, d, J = 7.0 Hz), 3.30 (3H, s), 2.92 (1H, t, J = 6.9 Hz); ^{13}C NMR (CD_3COCD_3) δ 136.6, 113.9, 112.9, 68.9, 59.4, 59.3, 58.5, 48.2.

(3aα,4α,7α,7aα,8*r*)- (50) and (3aα,4α,7α,7aα,8*s*)-3a,4,7,7a-Tetrahydro-8-(methoxymethyl)-4,5,6,7,8-pentamethyl-2-phenyl-4,7-methano-1,3(2*H*)-isoindole-1,3-dione (51). Anti adduct **50**: white solid; mp 105−106 °C; ^{1}H NMR δ 7.38 (3H, m), 7.06 (2H, d, J = 7.1 Hz), 3.22 (3H, s), 3.16 (2H, s), 3.09 (2H, s), 1.63 (6H, s), 1.33 (6H, s), 0.95 (3H, s); ^{13}C NMR δ 176.8, 135.4, 132.0, 129.1, 128.3, 126.6, 75.0, 67.6, 59.7, 59.2, 51.5, 12.9, 12.7, 11.5. Syn adduct **51** (from mixture): ^{1}H NMR δ 7.38 (3H, m), 7.06 (2H, m), 3.31 (3H, s), 3.23 (2H, s), 3.18 (2H, s), 1.58 (6H, s), 1.34 (6H, s), 0.79 (3H, s).

(1α,4α,4aα,9aα,11*r*)- (52) and (1α,4α,4aα,9aα,11*s*)-1,4,4a,9a-Tetrahydro-11-(methoxymethyl)-1,2,3,4,11-pentamethyl-1,4-methanoanthracene-9,10-dione (53). Anti adduct **52**: yellow solid; mp 132−136 °C; ^{1}H NMR δ 7.92 (2H, m), 7.63 (2H, m), 3.19 (3H, s), 3.17 (2H, s), 3.12 (2H, s), 1.24 (6H, s), 1.10 (6H, s), 0.94 (3H, s); ^{13}C NMR δ 198.1, 136.6, 135.6, 133.3, 125.7, 74.7, 63.8, 63.6, 59.2, 55.5, 13.0, 11.4, 11.8. Syn adduct **53** (from mixture): ^{1}H NMR δ 7.92 (2H, m), 7.63 (2H, m), 3.31 (3H, s), 3.26 (2H, s), 3.22 (2H, s), 1.27 (6H, s), 1.06 (6H, s), 0.74 (3H, s).

(10*r*)- (54) and (10*s*)-5,8-Dihydro-10-(methoxymethyl)-5,6,7,8,10-pentamethyl-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (55). Anti adduct **54**: ^{1}H NMR δ 7.36 (5H, m), 3.23 (3H, s), 3.04 (2H, s), 1.77 (6H, s), 1.68 (6H, s), 1.19 (3H, s); ^{13}C NMR δ 159.2, 132.6, 131.4, 129.0, 128.1, 125.4, 81.2, 74.3, 63.4, 59.4, 13.1, 11.6, 11.2. Syn adduct **55**: white solid; mp 134−134.5 °C; ^{1}H NMR δ 7.36 (5H, m), 3.50 (2H, s), 3.35 (3H, s), 1.73 (6H, s), 1.70 (6H, s), 0.80 (3H, s); ^{13}C NMR δ 159.2, 132.8, 131.4, 129.0, 128.1, 125.4, 81.3, 73.6, 62.3, 59.3, 12.0, 11.4, 11.2.

(7*r*)- (56) and (7*s*)-2,3-Dicarbomethoxy-7-(methoxymethyl)-1,4,5,6,7-pentamethylbicyclo[2.2.1]hepta-2,5-diene (57). Anti adduct **56**: yellow oil; ^{1}H NMR δ 3.73 (6H, s), 3.30 (2H, s), 3.21 (3H, s), 1.67 (6H, s), 1.22 (6H, s), 1.11 (3H, s); ^{13}C NMR δ 166.4, 153.3, 143.0, 83.2, 76.4, 65.9, 59.2, 51.7, 14.0, 11.8, 9.5. Syn adduct **57** (from mixture): ^{1}H NMR δ 3.75 (6H, s), 3.46 (2H, s), 3.26 (3H, s), 1.63 (6H, s), 1.22 (6H, s), 0.96 (3H, s)

(7*r*)- (58) and (7*s*)-2,2,3,3-Tetracyano-7-(methoxymethyl)-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene (59). Anti adduct **58** (from mixture): ^{1}H NMR δ 3.23 (3H, s), 3.07 (2H, s), 1.87 (6H, s), 1.51 (6H, s), 1.40 (3H, s); ^{13}C NMR δ 141.7, 111.4, 111.0, 75.8, 73.1, 68.2, 65.3, 59.5, 14.9, 12.2, 10.8. Syn adduct **59** (from mixture): ^{1}H NMR δ 3.61 (2H, s), 3.35 (3H, s), 1.83 (6H, s), 1.54 (6H, s), 0.97 (3H, s); ^{13}C NMR δ 141.4, 111.2, 111.0, 75.7, 73.1, 68.5, 64.3, 59.2, 15.8, 12.1, 10.7.

Acknowledgment. We are grateful to Dr. John N. Bridson of this Department for the X−ray structure determination. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Additional characterization data for adducts (IR, NOE data, MS or HRMS, elemental analysis); preparation of diene **41** and spectral data for its adducts with NPM, PTAD, and TCNE (**60**−**62**); ^{13}C NMR spectra of **3**, **7**, **8a**, **9a**, **10**−**23**, **29**, **31**, **33**, **35**, **37**, **45**, **46**, **48**−**50**, **52**, **54**−**56**, **58**; the X−ray structure of **35** (41 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9707949