Facial Selectivity in the Diels−Alder Reactions of 5-Chloro-, 5-Bromo-, and 5-Iodo-1,3-cyclopentadiene and Derivatives

Mark A. Wellman, Lori C. Burry, Johnathon E. Letourneau, John N. Bridson,[†] David O. Miller, and D. Jean Burnell*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada

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A variety of dienophiles was used to assess the facial selectivity of Diels−Alder reactions in a series of 1,3-cyclopentadiene derivatives (**1**−**3**, **6**−**10**) in which chlorine, bromine, and iodine were plane-nonsymmetric atoms pitted against hydrogen or methyl at C-5. The results were rationalized in terms of the major factor controlling the facial selectivity being related to steric hindrance between the diene and the dienophile. Selectivity did not correlate with reactivity. Facial selectivity in the reactions with 4-phenyl-1,2,4-triazoline-3,5-dione as the dienophile was also influenced by a second significant factor, postulated to be filled-orbital repulsion with the halogen substituent.

Introduction

There are many examples of facial selectivity in Diels−Alder reactions involving plane-nonsymmetric cyclopentadienes.[1] The published precedent indicates that cyclopentadienes substituted at C-5 with fluorine,[2] oxygen,[3] or nitrogen[4] all add dienophiles very predominantly syn to the heteroatom. Indeed, even when the C-5 substituent is an sp^3-hybridized carbon, there are instances in which a preference for addition syn to carbon have been reported,[5] and a number of more complex carbon-substituted examples have also been studied.[6] Substitution with sulfur leads to Diels−Alder reactions with little facial selectivity, and larger substituents give anti-addition products predominantly.[4,7]

We have proposed, on the basis of an ab initio computational study,[8] that it is the syn-versus-anti difference in the energy required to deform the two addends into their transition-state geometries that is the major contributor to facial selectivity in the reactions of all the simpler cyclopentadienes. Computational work requires reliable, experimental selectivity data for comparison, and further efforts on the computational side are now hampered by inconsistencies and shortcomings in the experimental data for the simplest dienes. Chlorine-substituted dienes are of particular interest because in the ab initio work the reaction of the simple 5-substituted chloro diene **1** was the only instance in which deformation of the dienophile (ethylene) was a major factor in the determining facial selectivity, which was calculated to be 73% syn to the chlorine.[8] The facial selectivity in Diels−Alder reactions involving **1** have been reported twice. Breslow and co-workers[9] indicated that with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) the product was a mixture, and it was implied that the anti-addition product was the major adduct. On the other hand, Franck-Neumann and Sedrati[10] reported that **1** showed a modest preference (ratio 1.5:1) for syn-addition with dimethyl acetylenedicarboxylate. The pentachloro diene **2** offers the same facial alternative as **1**, but **2** is obviously electronically quite different. Williamson and co-workers[11] claimed that maleic anhydride reacted with **2** 91% syn to the chlorine, and this reaction became almost facially specific when catalyzed by $AlCl_3$. Furthermore, they reported a range of facial selectivities when **2** reacted with different dienophiles,[11] as Ishida *et al.*[7d] have recently done with a sulfur-substituted cyclopentadiene. The pentamethyl derivative **3** added maleic anhydride exclusively syn to the chlorine,[4] but this facial selectivity is helped by the fact that, with many dienophiles, **4** directs addition mainly anti to the C-5 methyl group.[12] In contrast to Williamson's and Ishida's results, we recently reported that facial selectivity with **5** showed

[†] Author to whom correspondence regarding X-ray crystal structures should be addressed.

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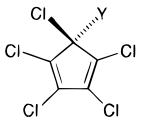
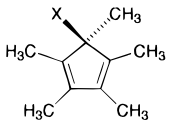
no dependence on the nature of the dienophile: addition was exclusively anti to chlorine.[13]

1 X = Cl
7 X = Br
8 X = I
55 X = SPh



2 Y = H
5 Y = OCH_3
6 Y = CH_3



3 X = Cl
4 X = H
9 X = Br
10 X = I

Systematic experimental results with chlorine-substituted dienes are clearly required. In this paper, the reactions of chloro diene **1** are reported with different dienophiles, and we reevaluate some of the previously reported[11] reactions of **2**. We also extend the data for **3** to other dienophiles, and, to complement this work with a diene electronically related to **2**, we assess for the first time the facial selectivity of reactions involving the pentachloro methyl diene **6**.

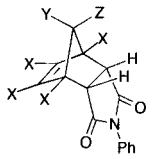
Cyclopentadienes substituted with bromine and iodine have received little attention and need to be examined more thoroughly. It had been implied that anti addition was the exclusive mode of cycloaddition with dienes **7** and **8**, in spite of yields of less than 40% for the adducts.[9,10,14] However, our calculations suggested that some syn-addition products should be found with **7**, although we agree that the facial selectivity of **8** should be extremely high.[8] Thus, we have also measured facial selectivities for dienes **7** and **8** as well as the pentamethyl dienes **9** and **10**, which might be expected to have a better chance of providing mixtures of syn and anti adducts of measurable proportions.

Results and Discussion

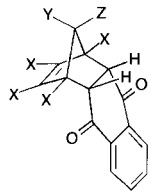
The simple 5-chloro-, 5-bromo-, and 5-iodo-1,3-cyclopentadienes (**1**, **7**, and **8**) are known compounds, which were prepared from cyclopentadienylthallium and the corresponding *N*-halosuccinimide.[9,14] Because of possible complications arising from dimerization or isomerization of the dienes to plane-symmetric 1- and 2-halo-1,3-cyclopentadienes by a 1,5-sigmatropic mechanism,[9] solutions of the dienes were added directly to cool solutions of dienophiles. Three dienophiles of very different characteristics were employed. *N*-Phenylmaleimide (NPM) is a relatively reactive ethylene derivative, which was likely to best mimic the simple dienophile (ethylene itself) used in our initial computational work.[8] 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD)[15] is a reactive, heteroatomic dienophile that resembles NPM in its nonreacting portion. It has been implicated in nonconcerted Diels–Alder reactions.[16] Tetracyanoethylene (TCNE) is the most reactive dienophile,[17] but also more sterically demanding than either NPM or PTAD in the exo-region of its Diels–Alder transition state.

1,2,3,4,5-Pentachloro-1,3-cyclopentadiene (**2**) was prepared by a procedure based on that of McBee and Smith.[18] Deprotonation of **2** with *n*-butyllithium followed by addition of CH_3I gave the methyl analog **6**. Diene **2** would also dimerize on standing, but this was less of a problem than with **1**. In order to compare our results fairly with those of Williamson and co-workers,[11] maleic anhydride (MA) and styrene were also used as dienophiles with the polychlorinated dienes **2** and **6**. Production of the pentamethyl dienes **3**, **9**, and **10** was by trapping the pentamethylcyclopentadienyl anion with the appropriate electrophile: NCS, NBS, or I_2. It should be noted that chlorination of **4** was not an efficient process, and diene **3** was always contaminated with **4**, which was inseparable without considerable losses. Therefore, reactions involving **3** were always carried out with a mixture of **3** and **4**, but, as we had spectra for the adducts derived from **4** in hand,[12] the analysis of the adduct mixtures was still straightforward. Dienes **3**, **9**, and **10** were reacted with the same three dienophiles as were used with **1**, **7**, and **8**.

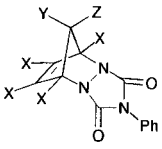
After an appropriate reaction time, the solvents were evaporated from the reaction mixtures. Adduct ratios were determined by careful integration of the ^1H NMR spectra of these crude mixtures, but, in most instances, it was also evident from the simplicity of these spectra that the very predominant process was the Diels–Alder reaction; i.e., the degree of chemical transformation was very high. Also, every adduct (**11**–**31**, **33**, **35**–**54**)



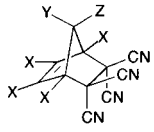
11 X = H, Y = H, Z = Cl
12 X = H, Y = Cl, Z = H
19 X = Cl, Y = H, Z = Cl
20 X = Cl, Y = Cl, Z = H
27 X = CH_3, Y = CH_3, Z = Cl
31 X = Cl, Y = CH_3, Z = Cl
39 X = H, Y = H, Z = Br
40 X = H, Y = Br, Z = H
44 X = CH_3, Y = CH_3, Z = Br
45 X = CH_3, Y = Br, Z = CH_3
49 X = H, Y = I, Z = H
52 X = CH_3, Y = I, Z = CH_3



13 X = H, Y = H, Z = Cl
14 X = H, Y = Cl, Z = H
28 X = CH_3, Y = CH_3, Z = Cl



15 X = H, Y = H, Z = Cl
16 X = H, Y = Cl, Z = H
25 X = Cl, Y = H, Z = Cl
26 X = Cl, Y = Cl, Z = H
29 X = CH_3, Y = Cl, Z = CH_3
37 X = Cl, Y = CH_3, Z = Cl
38 X = Cl, Y = Cl, Z = CH_3
41 X = H, Y = H, Z = Br
42 X = H, Y = Br, Z = H
46 X = CH_3, Y = Br, Z = CH_3
50 X = H, Y = I, Z = H
53 X = CH_3, Y = I, Z = CH_3



17 X = H, Y = H, Z = Cl
18 X = H, Y = Cl, Z = H
30 X = CH_3, Y = CH_3, Z = Cl
43 X = H, Y = Br, Z = H
47 X = CH_3, Y = CH_3, Z = Br
48 X = CH_3, Y = Br, Z = CH_3
51 X = H, Y = I, Z = H
54 X = CH_3, Y = I, Z = CH_3

derived from dienes **1**–**3** and **6**–**10** arose by reaction with the intended diene, not a plane-symmetric isomer resulting from a 1,5-sigmatropic rearrangement. There were two exceptions. The NMR spectra of the crude products

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Table 1. Relative Amounts (%) of the Anti-Adducts from the Reactions of Chlorine-Substituted Dienes with Various Dienophiles

	dienophile					
diene	NPM	MA	NQ	styrene	PTAD	TCNE
1	21		28		58	70
2	42	37	40[a]	67	78	
3	0	0[b]	0		100	0
6	0	0		25	81	

[a] The result is for 1,4-benzoquinone, ref 11a. [b] Reference 4.

Table 2. Relative Amounts (%) of the Anti-Adducts from the Reactions of Bromine- and Iodine-Substituted Dienes with Three Dienophiles

	dienophile		
diene	NPM	PTAD	TCNE
7	85	96	100
9	50	100	95
8	100	100	100
10	100	100	100

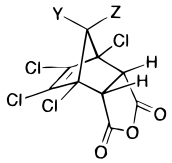
of the reactions of **6** with NPM and with MA showed two sets of adduct signals, but the minor adducts proved to be unsymmetrical (tentatively **32** and **34**). Facial selectivities with the chlorine-substituted dienes are summarized in Table 1, and selectivities with the bromine- and iodine-substituted dienes are found in Table 2. Some effort was made to obtain a sample of each adduct in a form that was homogeneous by NMR; therefore, almost every adduct mixture was subjected to chromatography. This was successful in most instances in which an adduct was produced in a reasonable proportion. For many adducts, the relative stereochemistry was determined by measurement of NOE's in the ^{1}H NMR spectra of the homogeneous adducts. Nevertheless, single-crystal X-ray structure determinations[19] were performed on 13 adducts for which NOE's were either ambiguous or impossible. For some of the less stable adducts we had to rely on an analysis of trends in the NMR spectra in order to infer the stereochemistry.

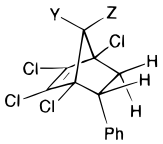
An effort was also made to verify that adduct ratios were the result of kinetically controlled processes. Isolated adducts were heated for long periods at or above the temperatures used for their formation, sometimes in the presence of a surrogate dienophile. In no instance was there a hint of the development of symmetrical or unsymmetrical isomeric adducts, or of dimers of the diene, or of products derived from surrogate dienophiles.

In the Diels−Alder reactions of the 1,3-cyclopentadiene derivatives under study, there must be a steric interaction between the incoming dienophile and the syn-substituent at C-5 of the diene, but our computational work suggested that the facial selectivity comes from the energy required to deform the addends into their transition-state geometries.[8] It seems that at the transition state the steric hindrance has been translated largely into this deformation because the calculations indicated very little interaction energy (between the dienophile and the diene) at the transition state. Thus, we propose that, with 5-substituted 1,3-cyclopentadienes, facial selectivity can be traced back mainly to the difference in the magnitudes of the dienophile−diene steric interactions, syn versus anti.

(19) Atomic coordinates for the X-ray structures of **16**, **18**, **26**, **27**, **29**, **30**, **38**, **42**, **43**, **48**, **49**, **50**, and **51** 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.

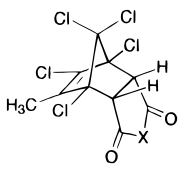
Calculations predicted that ethylene should add to diene **1**, via C_S-constrained transition states, preferentially to the face syn to the chlorine, i.e., only 27% anti-addition.[8] Our experiments with the ethylenic dienophiles NPM and NQ gave exellent agreement with this calculated selectivity (Table 1). If the reason for the facial selectivity was largely steric, then the pentachloro diene **2** should react with selectivity similar to that of **1**. The selectivity that Williamson[11] reported for the reaction of **2** with MA was 9% anti (**21**), which was significantly more selective than the reaction of **1**. However, in our hands, **2** with MA and also with NPM showed selectivity more like that of **1** (Table 1). Our results were in fact similar to the selectivity Williamson gave for **2** with another ethylenic dienophile, 1,4-benzoquinone (40% anti-adduct), and we conjecture that the slight attenuation of selectivity of **2** relative to **1** was due to the necessity of reacting **2** at higher temperatures or the fact that in the transition state for syn-addition with **2** the C-5 chlorine must become coplanar with four other chlorines, whereas in **1** the C-5 chlorine becomes coplanar with hydrogens. We noticed that **21** and **22** were sparingly soluble in $CDCl_3$. Hence, the ratio reported previously may have been colored by the relative solubilities of the adducts.





21 Y = H, Z = Cl
22 Y = Cl, Z = H
33 Y = CH_3, Z = Cl

23 Y = H, Z = Cl
24 Y = Cl, Z = H
35 Y = CH_3, Z = Cl
36 Y = Cl, Z = CH_3



32 X = N-Ph
34 X = O

With TCNE, two CN groups extend into the exo region of the Diels−Alder transition state, and these would be expected to interact unfavorably with a syn-chlorine on **1**. Indeed, with TCNE the major adduct **18** (70%) was the result of anti-addition. PTAD was expected to present less steric hindrance toward a syn-chlorine, but its reactions with both **1** and **2** suggested otherwise because their major adducts **16** and **26** were the results of anti-addition. The reason for this behavior became apparent from the reactions with dienes **3** and **6**, in which a C-5 chlorine was pitted against a methyl group. Diene **4** adds dienophiles mainly to its sterically less hindered face, anti to its C-5 methyl.[12] This, in concert with the tendency seen with **1** and **2** to add ethylenic dienophiles syn to the chlorine, resulted in additions of NPM, MA, and NQ exclusively syn to the chlorine with **3** and **6**. Whereas the selectivities of TCNE and PTAD were similar with **1**, these dienophiles showed dramatically opposite selectivities with **3**. TCNE, like the ethylenic dienophiles, added exclusively syn to the chlorine (**30**). PTAD added exclusively anti (**29**) to the chlorine of **3** and 81% anti (**38**) to the chlorine of **6**. From these results it was inferred that the reactions of PTAD were also

affected by a second phenomenon, which was not steric hindrance. The possibility of an attractive interaction between the C-5 hydrogen of **1** or **2** and a nitrogen lone-pair from PTAD, which might have enhanced anti-addition, was ruled out because in **3** and **6** the C-5 hydrogen had been replaced by a methyl group. What was consistent with these observations was either a destabilizing electrostatic interaction in the syn transition state, as might have been expected with a more ionic, less concerted mechanism,[16] or a filled-orbital repulsion of the type postulated by Coxon *et al.*[20]

The behavior of **2** and of **6** with styrene suggested that the filled-orbital explanation was more plausible. In contrast with the symmetrical dienophiles, styrene, which must react via an unsymmetrical transition state that also is likely to be asynchronous, reacted with **2** (via an endo transition state) mainly by anti-addition (**24**). Nevertheless, styrene gave only 25% anti-adduct (**36**) with **6**, completely in accord with an increase in the steric hindrance on the anti face. The same trend might have been expected if the selectivity with PTAD were the result of an asynchronous process.

As seen in Table 2, the Diels−Alder reaction of the bromine-substituted diene **7** with NPM was not stereospecific, 15% of the syn-adduct **39** was detected, but, with the more sterically demanding dienophile TCNE, all the product (**43**) was derived by anti-addition. PTAD again showed an aversion for addition syn to a lone-pair-bearing halogen in its reaction of **7**. The pentamethyl diene **9** displayed no facial selectivity whatsoever with NPM, indicating a fortuitous balance in the steric factors. Anti-adducts (**46** or **48**) predominated in the reactions of **9** with PTAD and TCNE. The results of additions with the iodine-substituted dienes **8** and **10** were not unexpected on the basis of the computational data.[8] Addition of every dienophile was exclusively anti, which showed that sterically even a methyl group was completely subjugated by iodine.

Recently, Inagaki and co-workers[7d] proposed that Diels−Alder reactions are members of a class of reactions in which reactivity enhances selectivity. To illustrate this phenomenon, they reported the facial selectivities of 5-(phenylthio)-1,3-cyclopentadiene (**55**) with MA, NPM, PTAD, and TCNE. Reactivity increased in that order, and so did the facial selectivity, from 55% anti-addition with MA up to 100% anti-addition with TCNE. The data in Table 1 do not correlate with reactivity, but it might be argued that rigorous rate data in these systems are not available. Thus, we decided to probe the reactivity−selectivity parameter in a different way. Two reactions were accelerated by catalysis. The reaction of **1** with NPM was carried out in the presence of 0.3 molar equiv of $SnCl_4$. The reaction was over very quickly, but the proportion of syn-adduct **11** increased very marginally, from 79% to only 81%. The $SnCl_4$-catalyzed reaction of **7** with NPM showed no significant change in the proportion of the anti-adduct **40**, which remained at 85%. Obviously, enhancement of selectivity by reactivity is either tiny or negligible in these reactions. In light of our work, Inagaki's data can be rationalized as follows: NPM and MA are similar in shape and similar in facial selectivity. TCNE is more sterically demanding than is NPM in the exo region, so syn-addition is discouraged, and the nitrogen lone-pairs of PTAD may resist addition syn to sulfur, a lone-pair-bearing group, just as we suggest occurred with the halogenated dienes.

Any rationalization based on steric hindrance must take into account two issues. The first is the "size" of the substituents, and the other is geometry. For these Diels−Alder reactions, using *A* values as a measure of steric hindrance would lead to no correlation with facial selectivity, because the geometry[8] of these Diels−Alder reactions is very different to that of axial substituents on cyclohexane. Simple van der Waals radii of the substituents do correlate with facial selectivity, with the exception of hydrogen. Hydrogen seems to exert a steric presence larger than its van der Waals radius would suggest, but the steric hindrance provided by a C−H bond, *which uniquely involves an sp³-to-s linkage*, may be more than a match for carbon bonds to the atoms that give syn-adducts, *viz.* C−F,[2] C−O,[3] C−N,[4] and, as we have shown, C−Cl. Prompted by the results reported here, we are using high-level ab initio methods to investigate the steric influences of these bonds in the Diels−Alder reaction as well as to clarify the source of PTAD's anti-directing factor.

Experimental Section

General Methods. *N*-Phenylmaleimide (NPM), 1,4-naphthoquinone (NQ), and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD)[15] were purified by sublimation under vacuum. All reactions were performed under nitrogen. Adducts were usually purified by flash chromatography on silica gel with elution with hexane containing an increasing proportion of EtOAc and then recrystallization. IR spectra (cm^{-1}) were recorded as casts. Absorption intensities: s, strong; m, medium; w, weak. ^1H NMR spectra were obtained at 300 MHz in $CDCl_3$ solution unless otherwise noted; chemical shifts are relative to internal TMS; *apparent* multiplicities are reported here because in many instances the signals are second order; standard abbreviations are used for multiplicities (nar = narrow). NOE measurements were made with difference spectra, using previously described parameters.[21] NOE data take this form: saturated signal (enhanced signal, enhancement). ^{13}C NMR spectra are at 75 MHz in $CDCl_3$ unless otherwise noted; chemical shifts are relative to a solvent resonance. MS data are *m/z* (% of largest peak).

1,2,3,4,5-Pentachloro-1,3-cyclopentadiene (2). A solution of hexachlorocyclopentadiene (20.4 g, 74.9 mmol) in acetone (8.0 mL) was cooled in an ice bath as a solution of $SnCl_2 \cdot H_2O$ (17.2 g, 76.7 mmol) in acetone (30 mL) was added at a rate such as to maintain the temperature of the diene solution in the 30−35 °C range. After addition was complete (approximately 10 min), the brown solution was stirred at rt for 1 h. The acetone was removed under vacuum, and the residue was taken up in CCl_4. This solution was washed with H_2O and brine and then dried over $CaCl_2$. Vacuum distillation (73−76 °C/4 Torr) provided **2** as a yellow liquid (12.1 g, 68%). IR: 2938 (m), 1603 (s). ^1H NMR: δ 4.75 (s). ^{13}C NMR: δ 129.6, 129.0, 60.2. MS: 244 (0.3), 242 (5), 240 (14), 238 (22) and 236 (14) all M^+, 207 (11), 205 (49), 203 (100), 201 (79), 171 (2), 169 (7), 167 (8), 135 (2), 133 (9), 131 (13), 98 (6), 96 (20), 61 (22), 60 (11).

1,2,3,4,5-Pentachloro-5-methyl-1,3-cyclopentadiene (6). A 2.5 M solution of *n*-butyllithium (2.21 mL, 5.53 mmol) in hexanes was added dropwise to a solution of **2** (1.01 g, 4.25 mmol) in dry THF (40 mL) at −78 °C. Iodomethane (0.35 mL, 5.5 mmol) was added, and the mixture was allowed to warm slowly to rt. The solution was concentrated under vacuum, and the brown residue was redissolved in CH_2Cl_2. The solution was washed with water and brine and then dried over anhydrous $MgSO_4$. Flash chromatography with hexane as the

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eluent gave **6** (0.719 g, 67%) as an orange oil. IR: 2983, 2929, 2859, 1601, 1569, 1437, 1374. ^{1}H NMR: δ 1.69 (s). ^{13}C NMR: δ 134.3, 127.4, 69.7, 23.8. MS: 258 (1), 256 (7), 254 (24), 252 (34) and 250 (22) all M^+, 239 (3), 237 (5), 235 (3), 223 (0.5), 221 (10), 219 (48), 217 (100), 215 (75), 186 (3), 184 (24), 182 (76), 180 (79), 149 (0.7), 147 (5), 145 (16), 143 (10), 109 (23), 108 (17), 74 (26).

(3aα,4α,7a,7aα,8*r*)- (11) and (3aα,4α,7α,7aα,8*s*)-8-Chloro-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (12). A solution of cyclopentadienylthallium (0.576 g, 2.14 mmol) and *N*-chlorosuccinimide (0.293 g, 2.14 mmol) in ether (20 mL) under N_2 was stirred in an ice bath for 1 h. While still cool, the resulting suspension was filtered quickly through a plug of glass wool into a solution of NPM in C_6H_6 (10 mL). The stirred solution was returned to the ice bath for 12 h before being allowed to warm to rt. The solution was concentrated under vacuum to provide a cream-colored solid. Flash chromatography provided a sample of each adduct, 0.216 g (37%) of **11** and 0.074 g (13%) of **12**, for spectroscopic analysis. Syn-adduct **11** (colorless solid from EtOAc/hexane). Mp: 166−167.5 °C. IR: 1711. ^{1}H NMR: δ 7.44−7.37 (3H, m), 7.14 (2H, br d, J = 8.2 Hz), 6.32 (2H, t, J = 2.2 Hz), 4.07 (1H, br t, J = 1.6 Hz), 3.81 (2H, dd, J = 1.6, 3.0 Hz), 3.48 (2H, m). NOE data: 6.32 (7.14, 0.5%; 4.07, 1.3%; 3.48, 3%), 4.07 (6.32, 0.7%; 3.48, 3%), 3.81 (3.48, 4%), 3.48 (6.32, 3%; 4.07, 7%; 3.81, 4%). ^{13}C NMR: δ 176.1, 134.7, 131.7, 129.1, 128.7, 126.5, 70.8, 50.3, 43.7. MS (GC-MS): 275 (7) and 273 (21) both M^+, 238 (1), 210 (1), 174 (12), 173 (100), 145 (4), 129 (17), 126 (4), 119 (27), 103 (8), 100 (6), 91 (43), 77 (10), 65 (23), 54 (12). HRMS calcd for $C_{15}H_{12}{}^{35}ClNO_2$: 273.0556, found 273.0547.

Anti-adduct **12** (colorless solid). Mp: 169.5−171 °C. IR: 1719. ^{1}H NMR: δ 7.47−7.38 (3H, m), 7.13 (2H, br d, J = 6.9 Hz), 6.26 (2H, nar m), 4.06 (1H, nar m), 3.64 (2H, nar m), 3.45 (2H, dd, J = 1.6, 3.0 Hz). NOE data: 6.26 (7.13, 0.6%; 3.64, 3%), 4.06 (3.64, 3%; 3.45, 4%), 3.64 (6.26, 3%; 4.06, 4%; 3.45, 1.3%), 3.45 (7.13, 0.5%; 4.06, 10%; 3.64, 4%). ^{13}C NMR: δ 174.9, 131.6, 129.2, 128.8, 126.5, 72.5, 51.5, 42.8. MS (GC−MS): 275 (8) and 273 (25) both M^+, 238 (1), 210 (1), 174 (23), 173 (100), 145 (4), 129 (19), 126 (14), 119 (27), 103 (9), 100 (14), 91 (47), 77 (12), 65 (28), 54 (14). HRMS calcd for $C_{15}H_{12}{}^{35}ClNO_2$: 273.0556, found 273.0549.

(1α,4α,4aα,9aα,11*r*)- (13) and (1α,4α,4aα,9aα,11*s*)-11-Chloro-1,4,4a,9a-tetrahydro-1,4-methanoanthracene-9,-10-dione (14). The same procedure as for **11**/**12** was followed except that NQ was used as the dienophile. The adducts decomposed rapidly; thus, the ^{1}H NMR data are nonaromatic signals from crude adduct mixtures. Syn-adduct **13**. ^{1}H NMR: δ 6.13 (2H, t, J = 2.1 Hz), 3.81 (1H, t, J = 1.8 Hz), 3.63 (2H, dd, J = 1.6, 2.4 Hz), 3.50 (2H, nar m). Anti-adduct **14**. ^{1}H NMR: δ 6.09 (2H, nar m), tentatively 3.81 (1H, nar m, probably coincident with the corresponding signal for **13**), 3.66 (2H, nar m), 3.35 (2H, nar m).

(10*s*)- (15) and (10*r*)-10-Chloro-5,8-dihydro-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (16). The same procedure as for **11**/**12** was followed except that PTAD was used as the dienophile. Syn-adduct **15** (colorless solid). Mp: 175.5−176 °C. IR: 1725. ^{1}H NMR: δ 7.47−7.38 (5H, m), 6.56 (2H, t, J = 2.1 Hz), 5.05 (2H, nar m), 4.23 (1H, t, J = 1.3 Hz). NOE data: 6.56 (5.05, 3%; 4.23, 1.4%), 4.23 (6.56, 0.5%; 5.05, 3%). ^{13}C NMR: δ 158.0, 132.8, 129.2, 128.6, 125.6, 67.8, 65.6. MS: 277 (12) and 275 (36) both M^+, 240 (100), 214 (2), 156 (4), 121 (32), 119 (63), 102 (17), 100 (56), 91 (23), 78 (28), 65 (41), 64 (17). HRMS calcd for $C_{13}H_{10}{}^{35}ClN_3O_2$: 275.0461, found 275.0453.

Anti-adduct **16** (colorless crystals from EtOAc/hexane). Mp: 166.5−167.5 °C. IR: 1719. ^{1}H NMR: δ 7.47−7.34 (5H, m), 6.47 (2H, dt, J = 0.6, 1.8 Hz), 5.11 (2H, q, J = 1.8 Hz), 4.56 (1H, nar m). ^{13}C NMR: δ 157.9, 129.2, 129.0, 128.7, 125.5, 78.5, 66.4. MS: 277 (14) and 275 (41) both M^+, 240 (42), 214 (2), 158 (8), 156 (24), 121 (52), 119 (93), 102 (31), 100 (100), 91 (27), 78 (22), 65 (58), 64 (20). HRMS calcd for $C_{13}H_{10}{}^{35}ClN_3O_2$: 275.0461, found 275.0453. Anal. Calcd for $C_{13}H_{10}ClN_3O_2$: C, 56.72; H, 3.63; N, 15.27, found C, 56.66; H, 3.69; N, 15.36. The structure of **16** was confirmed by X-ray crystallography.[19]

(7*r*)- (17) and (7*s*)-7-Chlorobicyclo[2.2.1]hept-5-ene-2,2,3,3-tetranitrile (18). The same procedure as for **11**/**12** was followed except that TCNE was used as the dienophile. Syn-adduct **17** (white solid). Mp: 200−201 °C. IR: 2254. ^{1}H NMR: δ 6.79 (2H, t, J = 2.2 Hz), 4.35 (1H, t, J = 1.5 Hz), 4.04 (2H, nar m). NOE data: 6.79 (4.35, 0.5%; 4.04, 2%), 4.35 (6.79, 0.5%). ^{13}C NMR (CD_3COCD_3): δ 140.0, 113.0, 111.8, 66.2, 59.6, 46.3. MS: no M^+, 201 (1), 193 (3), 166 (7), 139 (4), 129 (2), 128 (3), 102 (31), 100 (100), 76 (9), 65 (23). HRMS calcd for $C_{11}H_5N_4$ (M^+ − Cl): 193.0514, found 193.0506.

Anti-adduct **18** (colorless crystals from hexane/CH_2Cl_2). Mp: 206−207.5 °C. IR: 2255. ^{1}H NMR: δ 6.69 (2H, nar m), 4.52 (1H, nar m), 4.09 (2H, q, $J \approx$ 1.8 Hz). ^{13}C NMR (CD_3COCD_3): δ 136.2, 112.7, 111.9, 68.1, 60.8, 46.0. MS: no M^+, 201 (1), 193 (5), 166 (10), 139 (4), 129 (2), 128 (4), 102 (38), 100 (100), 76 (11), 65 (30). HRMS calcd for $C_{11}H_5N_4$ (M^+ − Cl): 193.0514, found 193.0514. The structure of **18** was determined by X-ray crystallography.[19]

(3aα,4*β*,7*β*,7aα,8*s*)- (19) and (3aα,4*β*,7*β*,7aα,8*r*)-4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1*H*-isoindole-1,3-dione (20). Diene **2** (3 equiv) and NPM in C_6H_6 were refluxed for 12 h. Sparingly soluble syn-adduct **19** (colorless crystals from acetone). Mp: 286−287 °C. IR: 1715. ^{1}H NMR: δ 7.48−7.44 (3H, m), 7.16 (2H, m), 4.33 (1H, s), 4.00 (2H, s). ^{13}C NMR: δ 169.7, 131.7, 130.7, 129.3, 129.2, 126.4, 80.2, 78.4, 52.6. MS: 417 (1), 415 (6), 413 (17), 411 (27), 409 (17) all M^+, 242 (2), 240 (6), 238 (10), 236 (6), 233 (1), 231 (7), 229 (14), 227 (11), 205 (4), 203 (8), 201 (6), 173 (100), 119 (23), 91 (17), 54 (17). HRMS calcd for $C_{15}H_8{}^{37}Cl^{35}Cl_4NO_2$: 410.8968, found 410.8949. Anal. Calcd for $C_{15}H_8Cl_5NO_2$: C, 43.78; H, 1.96; N, 3.40. Found: C, 43.29; H, 1.89; N, 3.39.

Anti-adduct **20** (colorless crystals from hexane/MeOH). Mp: 221−223 °C. IR: 1722. ^{1}H NMR: δ 7.51−742 (3H, m), 7.16 (2H, m), 4.47 (1H, s), 3.78 (2H, s). NOE data: 4.47 (3.78, 6%), 3.78 (4.47, 14%). ^{13}C NMR: δ 169.1, 130.7, 130.0, 129.5, 126.4, 81.4, 74.6, 51.9. MS: 415 (2), 413 (6), 411 (8), 409 (5) all M^+, 242 (1), 240 (4), 238 (7), 236 (4), 231 (4), 229 (9), 227 (7), 205 (3), 203 (6), 201 (5), 173 (100), 119 (15), 91 (13), 54 (15). Anal. Calcd for $C_{15}H_8Cl_5NO_2$: C, 43.78; H, 1.96; N, 3.40. Found: C, 43.20; H, 2.02; N, 3.36.

(3aα,4*β*,7*β*,7aα,8*s*)- (21) and (3aα,4*β*,7*β*,7aα,8*r*)-4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoisobenzofuran-1,3-dione (22). Diene **2** and MA (1.5 equiv) in toluene was refluxed for 6 h and then at 70 °C for 2 days. Syn-adduct **21** (colorless solid from EtOAc/hexane). Mp: 211−212 °C. IR: 1864, 1788, 1588. ^{1}H NMR: δ 4.33 (1H, s), 4.14 (2H, s). [^{1}H NMR for corresponding diacid: δ 4.14 (1H, s), 4.01 (2H, s).] ^{13}C NMR: δ 164.5, 132.3, 80.3, 73.4, 54.1. MS: 340 (2), 338 (7), 336 (11), 334 (6) all M^+, 303 (2), 301 (4), 299 (3), 261 (2), 259 (6), 257 (14), 255 (10), 244 (4), 242 (21), 240 (71), 238 (100), 236 (68), 233 (5), 231 (21), 229 (45), 227 (36), 207 (4), 205 (17), 203 (34), 201 (26), 259 (13), 157 (20), 96 (19). HRMS calcd for $C_9H_3{}^{35}Cl_4{}^{37}ClO_3$: 335.8495, found 335.8466. Anal. Calcd for $C_9H_3Cl_5O_3$: C, 32.14; H, 0.90. Found: C, 31.92; H, 0.95.

Anti-adduct **22** (from mixture containing **21** and MA). ^{1}H NMR: δ 4.45 (1H, s), 4.00 (2H, s). [^{1}H NMR of corresponding diacid: δ 4.32 (1H, s), 3.80 (2H, s). NOE data: 4.32 (3.80, 12%).]

(1*R,4*S**,5*S**,7*R**)- (23) and (1*R**,4*S**,5*S**,7*S**)-1,2,3,4,7-Pentachloro-5-phenylbicyclo[2.2.1]hept-2-ene (24).** Diene **2** and styrene (1.1 equiv) in *p*-xylene were refluxed at 100 °C for 12 h. Syn-adduct **23** (from mixture containing a small amount of a dimer of **2**). ^{1}H NMR: δ 7.35−7.29 (3H, m), 7.10 (2H, m), 4.18 (1H, d, J = 1.7 Hz), 3.96 (1H, dd, J = 4.4, 9.5 Hz), 2.90 (1H, dd, J = 9.5, 12.8 Hz), 2.40 (1H, ddd, J = 1.7, 4.4, 12.8 Hz). NOE data: 3.96 (7.10, 3%; 2.90, 4%). ^{13}C NMR: δ 134.4, 132.1, 131.9, 128.8, 128.4, 128.1, 77.9, 77.5, 72.7, 52.2, 40.8.

Anti-adduct **24**. Orange oil. IR: 3033 (m), 2924 (m), 1748 (m), 1599 (s), 1278 (s). ^{1}H NMR: δ 7.34 (3H, nar m), 7.10 (2H, nar m), 4.49 (1H, s), 3.72 (1H, dd, J = 4.9, 9.5 Hz), 2.74 (1H, dd, J = 9.5, 12.9 Hz), 2.58 (1H, dd, J = 4.9, 12.9 Hz). NOE data: 4.49 (3.72, 6%; 2.74, 2%), 3.72 (7.10, 4%; 4.49, 10%; 2.74, 4%). ^{13}C NMR: δ 134.8, 130.2, 129.8, 128.6, 128.4, 128.3, 81.2,

79.8, 74.1, 52.7, 41.7. MS: 342 (0.3, M^+), 240 (2), 238 (3), 236 (2), 205 (2), 203 (3), 201 (3), 125 (11), 104 (100), 103 (7), 78 (8), 77 (6).

(5*R*,8*S*,10*s*)- (25) and (5*R*,8*S*,10*r*)-5,6,7,8,10-Pentachloro-5,8-dihydro-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (26). Diene **2** and PTAD in C_6H_6 were warmed from rt to 70 °C. Syn-adduct **25** (beige crystals from petroleum ether/ether/MeOH). Mp: 160−165 °C dec. IR: 1805 (m), 1742 (s). ^{1}H NMR: δ 7.51−7.39 (3H, m), 7.32−7.25 (2H, m), 4.33 (1H, s). ^{13}C NMR: δ 155.4, 129.8, 129.5, 129.4, 125.5, 87.4, 74.7. MS: 415 (0.2), 413 (0.7), and 411 (0.2) all M^+, 244 (4), 242 (21), 240 (66), 238 (100), 236 (64), 207 (14), 205 (64), 203 (88), 202 (43), 201 (69), 119 (91), 91 (53), 64 (31). Anal. Calcd for $C_{13}H_6Cl_5N_3O_2$: C, 37.76; H, 1.46; N, 10.16. Found: C, 37.82; H, 1.49; N, 10.23.

Anti-adduct **26** (beige crystals from petroleum ether/ether/MeOH). Mp: 144−145, 148 °C dec. IR: 1806 (m), 1750 (s). ^{1}H NMR: δ 7.49−7.44 (3H, m), 7.32−7.27 (2H, m), 4.70 (1H, s). ^{13}C NMR: δ 155.2, 129.5 (many resonances), 128.0, 125.5, 89.2, 75.8. MS: 415 (2), 413 (3), and 411 (2) all M^+, 244 (1), 242 (7), 240 (21), 238 (33), 236 (21), 207 (5), 205 (24), 203 (48), 202 (3), 201 (36), 119 (100), 91 (80), 64 (43). Anal. Calcd for $C_{13}H_6Cl_5N_3O_2$: C, 37.76; H, 1.46; N, 10.16. Found: C, 37.53; H, 1.53; N, 10.14. The structure of **26** was determined by X-ray crystallography.[19]

(3aα,4α,7α,7aα,8*s*)-8-Chloro-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1*H*-isoindole-1,3-dione (27). A stirred solution of **4** (250 mg, 1.83 mmol) in THF (25 mL) was cooled in an ice bath as *n*-butyllithium (1.7 mL, 2.5 M in hexane) was added. The resulting slurry was stirred for 15 min before *N*-chlorosuccinimide (250 mg, 1.87 mmol) was added in one portion. After being stirred for 2 h at 0 °C, the mixture was diluted to two to three times the initial volume with ether, and this solution was washed with saturated aqueous $Na_2S_2O_3$ and H_2O. The organic solution was dried over $MgSO_4$, and the solvent was removed under vacuum. The residue was taken up in ether (15 mL), and NPM (260 mg, 150 mmol) was added. The solution was stirred at rt for 24 h. The solvent was removed under vacuum, and ^{1}H NMR analysis of the solid residue showed signals for only one adduct derived from **3** as well as signals for the adducts derived from **4**. Flash chromatography gave a homogeneous sample of syn-adduct **27** (colorless crystals). Mp: 184−185 °C. IR: 1713. ^{1}H NMR: δ 7.37 (3H, m), 7.06 (2H, d, J = 7.1 Hz), 3.42 (2H, s), 1.64 (6H, s), 1.43 (6H, s), 1.30 (3H, s). ^{13}C NMR: δ 176.3, 135.5, 131.9, 129.2, 128.5, 126.6, 92.6, 61.3, 51.5, 18.6, 11.6, 11.4. MS: 343 (9, M^+), 308 (3), 173 (8), 170 (100), 135 (43). HRMS calcd for $C_{20}H_{22}{}^{35}ClNO_2$: 343.1338, found 343.1339. The structure of **27** was determined by X-ray crystallography.[19]

(1α,4α,4aα,9aα,11*s*)-11-Chloro-1,4,4a,9a-tetrahydro-1,-2,3,4,11-pentamethyl-1,4-methanoanthracene-9,10-dione (28). The same procedure as for **27** was followed except that NQ was used as the dienophile. Syn-adduct **28** (colorless solid). Mp: 194−200 °C dec. IR: 1672. ^{1}H NMR (C_6D_6): δ 7.92 (2H, m), 7.08 (2H, m), 3.38 (2H, s), 1.39 (6H, s), 1.05 (3H, s), 0.95 (6H, s). ^{13}C NMR (C_6D_6): δ 195.9, 136.1, 135.3, 133.1, 125.8, 88.9, 64.0, 54.8, 17.7, 11.0, 10.7. MS: no M^+, 267 (3), 157 (15), 152 (100), 137 (49).

(10*r*)-10-Chloro-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 (29). The same procedure as for **27** was followed except that PTAD was used as the dienophile. Anti-adduct **29** (colorless crystals after preparative TLC). Mp: 127−127.5 °C. IR: 1726. ^{1}H NMR: δ 7.37 (5H, m), 1.79 (6H, s), 1.77 (6H, s), 1.59 (3H, s). ^{13}C NMR: δ 158.9, 133.1, 131.1, 129.1, 128.4, 125.4, 84.7, 81.1, 19.8, 11.3, 10.4. MS: 347 (1) and 345 (4) both M^+, 330 (3), 256 (5), 170 (100), 135 (32, 119 (16). HRMS calcd for $C_{18}H_{20}{}^{35}ClN_3O_2$: 345.1243, found 345.1242. The structure of **29** was determined by X-ray crystallography.[19]

(7*r*)-7-Chloro-2,2,3,3-tetracyano-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene (30). The same procedure as for **27** was followed except that TCNE was used as the dienophile. Syn-adduct **30** (colorless solid). Mp: 135 °C dec. IR: 2245. ^{1}H NMR: δ 1.90 (6H, s), 1.64 (6H, s), 1.39 (3H, s). NOE data: 1.90 (1.64, 0.9%; 1.39, 0.5%), 1.64 (1.90, 1.7%, 1.39, 2%), 1.39 (1.90, 0.3%; 1.64, 0.7%). ^{13}C NMR: δ 141.0, 111.3, 109.8, 83.0, 68.6, 50.9, 21.4, 12.4, 9.6. MS: no M^+, 263 (2), 170 (100), 135 (84), 119 (51). The structure of **30** was determined by X-ray crystallography.[19]

(3aα,4β,7β,7aα,8*s*)-4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-8-methyl-2-phenyl-4,7-methano-1*H*-isoindole-1,3-dione (31). Diene **6** and NPM (1.6 equiv) in C_6H_6 were refluxed for 6 days and then refluxed in toluene for 24 h. In the ^{1}H NMR spectrum, signals were present for a minor amount of an unsymmetrical adduct, likely **32**. Chromatography provided 75 mg (53%) of an off-white solid, still containing the unsymmetrical adduct, and recrystallization from CH_2Cl_2/hexane gave **31** as colorless needles (mp 207−209 °C) that were still contaminated with the second adduct, so spectral data are for these needles. IR: 1782 (m), 1721 (s). ^{1}H NMR: δ 7.48−7.37 (3H, m), 7.15−7.10 (2H, m), 4.06 (2H, s), 1.65 (3H, s). ^{13}C NMR: δ 170.1, 130.8, 130.5, 129.3, 129.2, 126.4, 91.6, 77.7, 53.6. MS: 431 (1), 429 (9), 427 (25), 425 (38), 423 (24) all M^+, 394 (0.9), 392 (5), 390 (10), 388 (8), 256 (2), 254 (8), 252 (12), 250 (7), 247 (3), 245 (14), 243 (29), 241 (22), 173 (100), 119 (98). HRMS calcd for $C_{16}H_{10}{}^{35}Cl_5NO_2$: 422.9153, found 422.9170. Anal. Calcd for $C_{16}H_{10}Cl_5NO_2$: C, 45.16; H, 2.37; N, 3.29. Found: C, 44.97; H, 2.41; N, 3.27. Readily discerned signals for putative **32**. ^{1}H NMR: δ 3.88 (1H, d, J = 7.5 Hz), 3.60 (1H, d, J = 7.5 Hz), 1.73 (3H, s). ^{13}C NMR: δ 51.4, 49.7, 11.7.

(3aα,4β,7β,7aα,8*s*)-4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-8-methyl-4,7-methanoisobenzofuran-1,3-dione (33). Diene **6** and MA (4 equiv) in toluene were refluxed for 8 days. In the ^{1}H NMR spectrum, signals were present for a minor amount of an unsymmetrical adduct, likely **34**. Syn-adduct **33** (from mixture containing small amount of **34**). Mp: 135 °C (sub). IR: 1852, 1783, 1594. ^{1}H NMR: δ 4.22 (2H, s), 1.63 (3H, s). ^{13}C NMR: δ 164.8, 131.0, 91.8, 77.6, 55.0, 18.7. MS (GC-MS): 352 (5), 350 (6), 348 (2) all M^+, 322 (4), 317 (8), 315 (23), 313 (17), 256 (10), 252 (26), 252 (49), 250 (28), 247 (9), 245 (51), 243 (100), 241 (89), 219 (13), 217 (26), 216 (17), 215 (25), 209 (29), 207 (70), 205 (56), 172 (25), 171 (20), 170 (40), 86 (35), 85 (56). Signals for putative **34**. ^{1}H NMR: δ 4.06 (1H, d, $J \approx$ 7.5 Hz), 3.79 (1H, d, $J \approx$ 7.5 Hz), 1.72 (3H, s).

(1*R,4*S**,5*S**,7*R**)- (35) and (1*R**,4*S**,5*S**,7*S**)-1,2,3,4,7-Pentachloro-7-methyl-5-phenylbicyclo[2.2.1]hept-2-ene (36).** Diene **6** and styrene (3 equiv) in toluene were refluxed for 9 days. Syn-adduct **35** (colorless solid). Mp: 53−54 °C. IR: 3065, 3033, 2995, 2941, 2870, 1600, 1497, 1458, 1381. ^{1}H NMR: δ 7.36−7.28 (3H, m), 7.11 (2H, m), 4.07 (1H, dd, J = 4.2, 9.2 Hz), 2.97 (1H, dd, J = 9.2, 12.7 Hz), 2.41 (1H, dd, J = 4.2, 9.2 Hz), 1.63 (3H, s). NOE data: 4.07 (7.11, 2%; 2.97, 4%), 2.97 (4.07, 4%; 2.41, 11%), 2.41 (7.11, 2%; 2.97, 11%). MS: 358 (1), 356 (2), 354 (1) all M^+, 258 (2), 256 (14), 254 (44), 252 (59), 250 (44), 237 (1), 235 (5), 233 (19), 231 (34), 229 (25), 221 (4), 219 (16), 217 (33), 215 (26), 198 (21), 196 (52), 194 (55), 186 (4), 184 (9), 182 (27), 180 (23), 127 (19), 125 (71), 104 (100).

Anti-adduct **36** (colorless crystals from hexane/ether). Mp: 94−96 °C. IR: 3064, 3032, 2999, 2944, 2869, 1603, 1512, 1454, 1383. ^{1}H NMR: δ 7.36−7.31 (3H, m), 7.10 (2H, m), 3.65 (1H, dd, J = 4.6, 9.1 Hz), 2.66 (1H, dd, J = 9.1, 13.2 Hz), 2.51 (1H, dd, J = 4.6, 13.2 Hz), 1.81 (3H, s). NOE data: 3.65 (2.66, 5%; 1.81, 1.6%), 2.66 (3.65, 2%; 2.51, 7%; 1.81, 0.7%), 2.51 (2.66, 9%), 1.81 (3.65, 8%; 2.66, 3%). MS: 358 (0.3), 356 (0.6), 354 (0.3) all M^+, 256 (2), 254 (7), 252 (12), 250 (8), 219 (2), 217 (4), 215 (3), 196 (2), 194 (2), 182 (3), 180 (3), 125 (21), 104 (100).

(5*R*,8*S*,10*s*)- (37) and (5*R*,8*S*,10*r*)-5,6,7,8,10-Pentachloro-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 (38). Diene **6** (0.167 g, and PTAD in C_6H_6 were refluxed for 12 h. Syn-adduct **37** (colorless crystals). Mp: 163−166 °C but first turning pink at 147 °C. IR: 1802 (m), 1749 (s). ^{1}H NMR: δ 7.50−7.42 (3H, m), 7.33−7.26 (2H, m), 1.63 (3H, s). ^{13}C NMR: δ 155.4, 129.8, 129.4, 128.1, 125.5, 91.4, 84.5, 19.4. MS: 429 (0.1), 427 (0.6), and 425 (0.1) all M^+, 394 (0.8), 392 (2), 390 (1), 275 (1), 273 (3), 271 (2), 258 (3), 256 (20), 254 (64), 252 (100), 250 (62), 223 (0.5), 221 (6), 219 (29), 217 (60), 215 (47), 186 (1), 184 (12), 182 (36), 180 (38), 119 (54), 91 (29), 64 (18). Anal. Calcd for

$C_{14}H_8Cl_5N_3O_2$: C, 39.33; H, 1.89; N, 9.83. Found: C, 39.25; H, 1.89; N, 9.92.

Anti-adduct **38** (colorless crystals). Mp: 129−131 °C but turning pink first at 125 °C. IR: 1805 (m), 1750 (s). ^{1}H NMR: δ 7.47−7.41 (3H, m), 7.31−7.27 (2H, m), 1.91 (3H, s). ^{13}C NMR: δ 155.3, 129.6, 129.5, 129.1, 125.5, 92.0, 86.4, 20.7. MS: 429 (0.9), 427 (2), and 425 (0.8) all M^+, 392 (0.8), 390 (0.4), 275 (0.6), 273 (2), 271 (1), 258 (3), 256 (20), 254 (64), 252 (100), 250 (63), 221 (5), 219 (21), 217 (44), 215 (34), 186 (0.8), 184 (8), 182 (25), 180 (26), 119 (38), 91 (21), 64 (13). Anal. Calcd for $C_{14}H_8Cl_5N_3O_2$: C, 39.33; H, 1.89; N, 9.83. Found: C, 39.34; H, 1.93; N, 10.03. The structure of **38** was determined by X-ray crystallography.[19]

(3aα,4α,7a,7aα,8*s*)- (39) and (3aα,4α,7α,7aα,8*r*)-8-Bromo-3a,4,7,7a-tetrahydro-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (40). The same procedure as for **11**/**12** was followed except that NBS was used as the halogen source. Syn-adduct **39** (colorless solid from CH_2Cl_2/hexane). Mp: 194.5−196 °C. IR: 1715. ^{1}H NMR: δ 7.47−7.37 (3H, m), 7.14 (2H, br d, J = 7.0 Hz), 6.32 (2H, t, J = 2.1 Hz), 4.15 (1H, t, J = 1.3 Hz), 3.88 (2H, dd, J = 1.8, 2.5 Hz), 3.52 (2H, m). NOE data: 6.32 (7.14, 0.8%; 4.15, 1.5%; 3.52, 3%), 4.15 (6.32, 0.6%; 3.52, 3%), 3.88 (3.52, 4%), 3.52 (6.32, 3%; 4.15, 6%; 3.88, 4%). ^{13}C NMR: δ 176.2, 135.2, 131.6, 129.1, 128.8, 126.5, 61.4, 50.7, 44.0. MS: 319 (23) and 317 (24) both M^+, 238 (9), 173 (100), 146 (7), 144 (7), 129 (16), 119 (11), 91 (33), 65 (32). HRMS calcd for $C_{15}H_{12}NO_2$ (M^+ − Br): 238.0867, found 238.0862.

Anti-adduct **40** (colorless solid from CH_2Cl_2/hexane). Mp: 188−189 °C. IR: 1716, 1594. ^{1}H NMR: δ 7.47−7.37 (3H, m), 7.12 (2H, br d, J = 7.0 Hz), 6.26 (2H, nar m), 4.06 (1H, br s), 3.66 (2H, m), 3.47 (2H, dd, J = 1.5, 2.9 Hz). NOE data: 6.26 (7.12, 1.1%; 3.66, 3%), 4.06 (3.66, 3%; 3.47, 5%), 3.66 (6.26, 4%; 4.06, 5%; 3.47, 3%), 3.47 (4.06, 9%; 3.66, 4%). ^{13}C NMR: δ 174.8, 132.5, 131.5, 129.1, 128.8, 126.4, 63.2, 51.9, 42.8. MS: 319 (63) and 317 (66) both M^+, 238 (19), 173 (100), 146 (5), 144 (5), 129 (11), 119 (6), 91 (12), 65 (33). HRMS calcd for $C_{15}H_{12}NO_2$ (M^+ − Br): 238.0867, found 238.0863.

(10*s*)- (41) and (10*r*)-10-Bromo-5,8-dihydro-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyradizine-1,3(2*H*)-dione (42). The same procedure as for **39**/**40** was followed except that PTAD was used as the dienophile. Syn-adduct **41**. ^{1}H NMR (nonaromatic signals from the adduct mixture): δ 6.53 (2H, br t, J = 2.1 Hz), 5.07 (2H, m), 4.27 (1H, nar m).

Anti-adduct **42** (colorless crystals from CH_2Cl_2/hexane). Mp: 170−170.5 °C. IR: 1719. ^{1}H NMR: δ 7.45−7.34 (5H, m), 6.47 (2H, dt, J = 0.5, 1.9 Hz), 5.15 (2H, q, J = 1.9 Hz), 4.51 (1H, nar m). ^{13}C NMR: δ 158.8, 130.9, 129.6, 129.2, 128.7, 125.4, 68.9, 55.2. MS: 321 (11) and 319 (12) both M^+, 240 (28), 202 (6), 200 (6), 177 (7), 146 (62), 144 (64), 121 (20), 119 (50), 91 (19), 78 (16), 65 (100), 64 (14). HRMS calcd for $C_{13}H_{10}N_3O_2$ (M^+ − Br): 240.0772, found 240.0757. The structure of **42** was determined by X-ray crystallography.[19]

(7*s*)-7-Bromobicyclo[2.2.1]hept-5-ene-2,2,3,3-tetranitrile (43). The same procedure as for **39**/**40** was followed except that TCNE was used as the dienophile. Anti-adduct **43** (colorless crystals from hexane/CH_2Cl_2). Mp: 215.5−217 °C. IR: 2254. ^{1}H NMR: δ 6.70 (2H, nar m), 4.48 (1H, br s), 4.13 (2H, nar m). ^{13}C NMR (CD_3COCD_3): δ 137.3, 113.0, 112.1, 61.4, 56.7, 45.9. MS: no M^+, 193 (5), 166 (12), 146 (73), 144 (75), 128 (10), 76 (17), 65 (100). HRMS calcd for $C_{11}H_5N_4$ (M^+ − Br): 193.0514, found 193.0515. The structure of **43** was determined by X-ray crystallography.[19]

(3aα,4α,7α,7aα,8*s*)- (44) and (3aα,4α,7α,7aα,8*r*)-8-Bromo-3a,4,7,7a-tetrahydro-4,5,6,7,8-pentamethyl-2-phenyl-4,7-methano-1*H*-isoindole-1,3-dione (45). The same procedure as for **27** was followed except that NBS was used as the halogen source. Syn-adduct **44** (colorless solid). Mp: 140−142 °C. IR: 1713. ^{1}H NMR (C_6D_6): δ 7.41 (3H, m), 6.99 (2H, d), 2.24 (2H, s), 1.49 (6H, s), 1.38 (6H, s), 1.11 (3H, s). NOE data: 2.24 (1.38, 0.7%; 1.11, 3%), 1.38 (2.24, 5%; 1.11, 2%), 1.11 (2.24, 11%; 1.49, 0.7%). ^{13}C NMR: δ 175.3, 137.7, 132.1, 129.2, 128.6, 126.5, 94.1, 61.5, 48.2, 21.7, 12.4, 11.6. MS: 389 (6) and 387 (6) both M^+, 308 (8), 216 (25), 214 (27), 173 (3), 135 (100).

Anti-adduct **45** (from the adduct mixture). ^{1}H NMR: δ 7.41 (3H, m), 7.05 (2H, m), 3.51 (2H, s), 1.65 (6H, s), 1.58, 6H, s), 1.49 (3H, s).

(10*r*)-10-Bromo-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 (46). The same procedure as for **44**/**45** was followed except that PTAD was used as the dienophile. Anti-adduct **46** (colorless crystals after preparative TLC). Mp: >95 °C dec. IR: 1778 (m), 1725 (s). ^{1}H NMR: δ 7.36 (5H, m), 1.82 (6H, s), 1.75 (6H, s), 1.74 (3H, s). ^{13}C NMR: δ 158.9, 134.2, 131.1, 129.1, 128.4, 125.4, 81.5, 21.7, 11.4, 11.1. MS: 391 (1) and 389 (1) both M^+, 256 (1), 216 (34), 214 (36), 135 (100). The structure of **46** was determined by X-ray crystallography.[19]

(7*r*)- (47) and (7*s*)-7-Bromo-2,2,3,3-tetracyano-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene (48). The same procedure as for **44**/**45** was followed except that TCNE was used as the dienophile. Syn-adduct **47** (from the adduct mixture). ^{1}H NMR: δ 1.91 (6H, s), 1.83 (6H, s), 1.66 (3H, s).

Anti-adduct **48** (colorless solid after preparative TLC). Mp: >150 °C dec. IR: 2248. ^{1}H NMR ($CDCl_3$/C_6D_6): δ 2.00/1.51 (3H, s), 1.86/2.29 (6H, s), 1.72/1.03. ^{13}C NMR: δ 144.2, 111.4, 111.1, 86.8, 69.0, 48.1, 24.0, 12.2, 10.1. MS: no M^+, 216 (13), 214 (16), 135 (100), 128 (59), 119 (25), 81 (2), 79 (7).

(3aα,4α,7α,7aα,8*r*)-3a,4,7,7a-Tetrahydro-8-iodo-2-phenyl-4,7-methano-1*H*-isoindole-1,3(2*H*)-dione (49). The same procedure as for **11**/**12** was followed except that *N*-iodosuccinimide was used as the halogen source. Anti-adduct **49** (colorless crystals from hexane/CH_2Cl_2). Mp: 211−212.5 °C. IR: 1707. ^{1}H NMR: δ 7.47−7.38 (3H, m), 7.12 (2H, br d, J = 6.9 Hz), 6.29 (2H, t, J = 1.8 Hz), 4.02 (1H, br s), 3.69 (2H, m), 3.57 (2H, dd, J = 1.5, 2.9 Hz). NOE data: 6.29 (7.12, 0.7%; 3.69, 4%), 4.02 (3.69, 3%; 3.57, 6%), 3.69 (6.29, 4%; 4.02, 5%; 3.57, 2%), 3.57 (4.02, 11%; 3.69, 5%). ^{13}C NMR: δ 174.7, 134.3, 131.4, 129.1, 128.8, 126.4, 53.4, 42.6, 41.0. MS: 365 (33, M^+), 238 (39), 210 (17), 192 (41), 174 (19), 173 (48), 129 (16), 119 (16), 95 (11), 91 (65), 69 (39), 65 (100), 57 (43), 55 (42). HRMS calcd for $C_{15}H_{12}NO_2$ (M^+ − I): 238.0867, found 238.0859. The structure of **49** was confirmed by X-ray crystallography.[19]

(10*r*)-5,8-Dihydro-10-iodo-2-phenyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (50). The same procedure as for **49** was followed except that PTAD was used as the dienophile. Anti-adduct **50** (colorless crystals from EtOAc/hexane). Mp: 133−134 °C. IR: 1713. ^{1}H NMR: δ 7.48−7.34 (5H, m), 6.47 (2H, t, J = 1.8 Hz), 5.16 (2H, q, J = 1.7 Hz), 4.41 (1H, br s). ^{13}C NMR: δ 157.6, 130.7, 129.1, 128.6, 125.4, 70.2, 30.0. MS: 367 (12, M^+), 254 (8), 241 (18), 240 (20), 192 (69), 177 (17), 151 (5), 121 (24), 119 (62), 93 (23), 91 (24), 79 (20), 65 (100), 64 (19). HRMS calcd for $C_{13}H_{10}IN_3O_2$: 366.9818, found 366.9799. The structure of **50** was determined by X-ray crystallography.[19]

(7*s*)-7-Iodobicyclo[2.2.1]hept-5-ene-2,2,3,3-tetranitrile (51). The same procedure as for **49** was followed except that TCNE was used as the dienophile. Anti-adduct **51** (colorless crystals after treatment with charcoal from hexane/CH_2Cl_2). Mp: 176 °C dec, 183−185 °C. IR: 2252. ^{1}H NMR: δ 6.71 (2H, nar m), 4.44 (1H, br s), 4.11 (2H, q, $J \approx$ 1.7 Hz). ^{13}C NMR (CD_3COCD_3): δ 139.1, 113.4, 112.2, 63.2, 44.9, 30.3. MS: 320 (8, M^+), 192 (47), 166 (4), 128 (13), 76 (13), 65 (100). HRMS calcd for $C_{11}H_5N_4$ (M^+ − I): 193.0514, found 193.0515. Anal. Calcd for $C_{11}H_5IN_4$: C, 41.28; H, 1.57; N, 17.50. Found: C, 41.27; H, 1.58; N, 17.68. The structure of **51** was determined by X-ray crystallography.[19]

(3aα,4α,7α,7aα,8*r*)-3a,4,7,7a-Tetrahydro-8-iodo-4,5,6,7,8-pentamethyl-2-phenyl-4,7-methano-1*H*-isoindole-1,3-dione (52). The same procedure as for **27** was followed except that I_2 was used as the halogen source. Anti-adduct **52** (pale yellow solid after preparative TLC, but still contaminated by some unreacted NPM). Mp: 105−108 °C. IR: 1717. ^{1}H NMR: δ 7.43 (3H, m), 7.04 (2H, d, J = 7.3 Hz), 3.13 (2H, s), 1.81 (3H, s), 1.60 (6H, s), 1.51 (6H, s). NOE data: 3.13 (1.81, 4%; 1.51, 1%), 1.81 (3.13, 12%; 1.51, 0.7%).^{13}C NMR: δ 175.1, 140.8, 134.1, 129.1, 128.6, 126.4, 86.4, 62.5, 45.9, 25.3, 14.0, 11.7. MS: 435 (1, M^+), 308 (14), 173 (100), 135 (35), 127 (2), 117 (22).

(10*r*)-5,8-Dihydro-10-iodo-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 (53). The same procedure as for **52** was followed except that PTAD was used as the dienophile. Anti-adduct **53** (gray solid). IR: 1777 (m), 1723 (s). ^{1}H NMR (C_6D_6): δ 7.40 (2H, m), 7.01 (2H, m), 6.90 (1H, m), 1.76 (6H, s), 1.75 (3H, s), 1.51 (6H, s). ^{13}C NMR (C_6D_6): δ 159.5, 136.6, 131.9, 129.4, 128.5, 126.0, 82.8, 69.8, 25.9, 12.9, 11.8.

(7*s*)-2,2,3,3-Tetracyano-7-iodo-1,4,5,6,7-pentamethylbicyclo[2.2.1]hept-5-ene (54). The same procedure as for **52** was followed except that TCNE was used as the dienophile. Anti-adduct **54** (gray solid). IR: 2247. ^{1}H NMR (C_6D_6): δ 1.75 (3H, s), 1.27 (6H, s), 1.10 (6H, s). ^{13}C NMR (C_6D_6): δ 147.8, 111.7, 111.1, 74.5, 70.2, 44.8, 28.0, 12.3, 11.6.

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Supporting Information Available: X-ray structures for **16**, **18**, **26**, **27**, **29**, **30**, **38**, **42**, **43**, **46**, and **49**−**51** and ^{13}C NMR spectra of **6**, **11**, **12**, **15**−**21**, **23**−**31**, **35**−**40**, **42**−**44**, **46**, and **48**−**54** (49 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.

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