Facial Selectivity in the Inverse-Electron-Demand Diels–Alder Reaction: Additions to 1,2,3,4,5-Pentachloro-5-methoxy-1,3-cyclopentadiene

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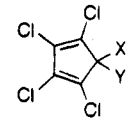
Received April 25, 1995®

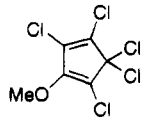
Dienophiles of various types underwent Diels–Alder cycloaddition to 1,2,3,4,5-pentachloro-5-methoxy-1,3-cyclopentadiene (**1**). Some reactions were predicted to proceed in the inverse-electron-demand mode whereas others were of the "normal" electronic configuration. The facial selectivity in every reaction was the same. Addition was exclusively to the face of **1** syn to its methoxy group. The facial selectivity was consistent with steric and/or torsional control of facial selectivity rather than a consequence of a stereoelectronic phenomenon.

Introduction

Facial selectivity in the Diels–Alder reactions of plane-nonsymmetric dienes[1] continues to be a topic of mechanistic debate. This selectivity has been rationalized in many ways. Steric,[2] torsional,[3] conformational,[4] and various stereoelectronic effects[2d,5] have been implicated. The latter have been particularly popular in rationalizing additions to C-5-heterosubstituted 1,3-cyclopentadienes, some of which react exclusively syn to the heteroatom.[5,6] Recently, we showed computationally that for the simple C-5-heterosubstituted 1,3-cyclopentadienes facial selectivity is largely the result of differences in the energy required to distort the addends, especially the diene, into the syn and anti transition state geometries.[7] However, both the experimental and the computational studies have concentrated on Diels–Alder reactions involving reactants with the "normal" electronic configuration, i.e., electron-rich dienes with electron-poor dienophiles. The few examples of facial selectivity in Diels–Alder reactions with "inverse-electron-demand" are thanks to work published more than 25 years ago by Williamson and co-workers.[8] We have examined the facial selectivity of the reactions of 1,2,3,4,5-pentachloro-5-methoxy-1,3-cyclopentadiene (**1**) with a number of dienophiles, and the results are presented below.



1 X = Cl, Y = OMe
2 X = Y = Cl
3 X = Y = OMe



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Results and Discussion

Diene **1** was obtained by slow addition of methanol containing a limiting amount of KOH to a solution of hexachlorocyclopentadiene **2**.[9] The yield of **1** was very poor, but this process avoided the production of the dimethoxy diene **3**, which proved to be very difficult to separate from **1** by chromatography. Diene **1** was in fact obtained as the major component of a 1.5:1 mixture that also contained the preparatively inseparable isomer **4**. However, this diene mixture could be used in the Diels–Alder study because, with a single exception, only adducts derived from **1** were detected, and **4** remained unchanged even after long reaction times.

Diene **1** reacted with electron-deficient ethylenic dienophiles (*N*-phenylmaleimide, 1,4-naphthoquinone), electron-rich ethylenic dienophiles (vinylene carbonate, ethoxyethylene), styrenes (styrene, 4-bromostyrene, 3-nitrostyrene, 2-vinylnaphthalene), a heteroatomic dienophile (4-phenyl-1,2,4-triazoline-3,5-dione), and an acetylenic dienophile (diethyl acetylenedicarboxylate). The electron-rich dienophiles and the styrenes reacted with **1** in the "inverse-electron-demand" mode, whereas the electron-

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® Abstract published in *Advance ACS Abstracts,* August 15, 1995.

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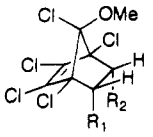
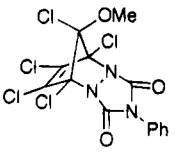
poor dienophiles reacted via the "normal" mode.[10] Adducts were not obtained in high yield, but reactions were usually terminated to preempt the buildup of troublesome side products. Facial selectivity in the reactions of **1** with every dienophile was very high: only one adduct derived from **1** was isolated (**5**–**14**), and this was the only



5 R_1, R_2 = -CO-NPh-CO-
6 R_1, R_2 = -CO-*o*-C_6H_4-CO-
7 R_1, R_2 = -O-CO-O-
8 R_1 = OEt, R_2 = H
9 R_1 = Ph, R_2 = H
10 R_1 = 4-BrPh, R_2 = H
11 R_1 = 3-NO_2Ph, R_2 = H
12 R_1 = 2-Naphthyl, R_2 = H



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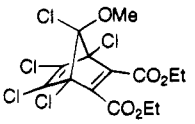

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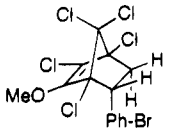
adduct detectable by ^{1}H NMR or GCMS in the crude reaction product, except in the following instance. With 4-bromostyrene two adducts were detected in the crude product, but the minor adduct **15** proved to be derived from **4**. A comparison of the ^{13}C NMR shifts for the adducts with those of adducts derived from **2** and **3**[9] did not reveal any trends that were useful for the assignment of stereochemistry. Nuclear Overhauser effects (NOE) were measured with **8**, **9**, **11**, and **12**, although the stereochemically diagnostic enhancements were small. Single-crystal X-ray analysis was necessary to establish the structures of adducts **5**–**7**, **10**, and **13**–**15** unequivocally.



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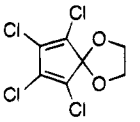
The fact that **1** did not react quickly with any of the dienophiles tested suggested that its rate of reaction was retarded very significantly, relative to 5-substituted 1,3-cyclopentadienes, probably by steric hindrance between the dienophile and the chlorines on the termini of the diene moiety of **1**.

It is more important to note that addition was to the face of **1** syn to its methoxy group, regardless of the dienophile used. Inverse-electron demand Diels–Alder reactions have not been addressed in the various rationalizations of facial selectivity, except by Williamson.[8] Nevertheless, the fact that the mode of reaction, "normal" or inverse-electron-demand, had no bearing on the facial selectivity with **1** is not what would be expected for stereoelectronic control of facial selectivity by mechanisms involving facial bias of the diene's π-system in terms of electron density[5b] or nucleophilicity,[5d,e] favorable mixing of a lone pair orbital of a heteroatom on the diene with an MO on the dienophile,[5a] or dipole–dipole[8] or electrostatic interactions.[5c] The facial selectivity with **1** was the same as that expected for the "normal" Diels–Alder reactions in which an oxygen function at C-5 of 1,3-cyclopentadiene very strongly directs addition syn to itself,[5f,6a,c,d] whereas chlorine is less selective.[5f,6e]

In an attempt to gain more information regarding the phenomenon controlling the facial selectivity, we determined in an approximate manner the relative rates of the reactions of **1**–**3**[9] with styrene[10] in a series of competitive reactions in boiling benzene. The reaction rates were 4:2:1, in the order **1** > **3** > **2**. The difference in rate between **3** and **2** did not reflect the high degree of facial selectivity shown by **1**, but this was likely due to a shortcoming of **3** as a model for one face of **1**.[11] Diene **16** may be a better model for the oxygen-bearing face of **1**, and **16**[9] reacted with styrene approximately 30 times faster than **2**. Thus, a diene with a chlorine in the anti position reacts more slowly than a diene with an oxygen in the anti position. It should be noted that this was not consistent with a popular hypothesis of facial selectivity through σ-donation by an anti substituent.[12]



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The facial selectivity of **1** and the relative rates are entirely consistent with the recently disclosed hypothesis, based on an ab initio computational study, that a second row atom on C-5 of 1,3-cyclopentadiene imparts a considerable degree of stabilization to the diene moiety in its deformed, transition state geometry only when addition is syn to these atoms, not anti.[7] The hypothesis was formulated from data for only the simple 5-substituted 1,3-cyclopentadienes, and the mechanism by which stabilization occurs is not clear. However, the realization that the hypothesis also holds for electronically different modes of reaction is important because this points to a mechanism for the stabilization that is not rooted in a stereoelectronic effect. Indeed, it suggests that the stabilization, and hence facial selectivity, in all cyclopentadiene derivatives is due mainly to steric or torsional considerations.

Experimental Section

General. All reactions were performed under nitrogen. IR spectra (cm^{-1}) were recorded as neat liquids. ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ solution unless otherwise noted; chemical shifts (δ) are relative to internal TMS, and coupling constants (J) are in Hz. NOE measurements were made with difference spectra, using previously described parameters,[13] on thoroughly degassed CD_2Cl_2 solutions at −60 °C. 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 (δ) are relative

(10) Calculation (ab initio 3-21G) of HOMO–LUMO gaps for the reactions of maleic anhydride and maleimide with **1**–**3** showed that "normal" reactions should be preferred, but the HOMO–LUMO gaps for the reactions of methoxyethylene and styrene with **1**–**3** were consistent with "inverse-electron-demand" reactions.

(11) Whereas the syn methoxy of **3** may assume an eclipsed conformation (i.e., dihedral angle of Me–O–C-5–O = 0°) to distance itself from the incoming dienophile, a 1,3-interaction of the methyls would mean that the anti methoxy would not be eclipsed. Therefore, at the transition state the anti methoxy would be close enough to the diene moiety to produce an unfavorable steric interaction.

(12) This is the application of the Cieplak mechanism to Diels–Alder reactions: (a) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540. (b) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447. Diels–Alder applications: refs 5f, 6g, and: (c) Chung, W.-S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 7882. (d) Halterman, R. L.; McCarthy, B. A.; McEvoy, M. A. *J. Org. Chem.* **1992**, *57*, 5585.

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to a solvent resonance. MS data are *m/z* (percent of largest peak). Diels–Alder reactions were followed by TLC; when the diene was largely consumed the solution was concentrated under vacuum and the residue was purified by flash column chromatography (elution with hexane containing an increasing proportion of EtOAc) and, in the case of solid adducts, recrystallization.

1,2,3,4,5-Pentachloro-5-methoxy-1,3-cyclopentadiene (1). A solution of **2** (6.8 g, 25 mmol) in dry THF (5.0 mL) was added at rt over 1 h to a solution of KOH (1.0 g, 18 mmol) in methanol (0.79 g, 25 mmol) and dry THF (5.0 mL). Stirring was continued for 3 h. The mixture was concentrated under vacuum, and the residue was taken up in CH_2Cl_2. The organic solution was washed with brine (2 × 20 mL), dried ($MgSO_4$), and concentrated under vacuum to give an orange oil. Flash chromatography (elution with hexane) provided (300 mg, 6%) of a yellow oil, which was a 1.5:1 mixture (by GCMS) of **1** and **4**, respectively. **1**. ^{1}H NMR: 3.61 (s). ^{13}C NMR: 130.5, 128.8, 98.4, 54.6. **4**. ^{1}H NMR: 4.21 (s).

(3aα,4α,7α,7aα,8*s*)-4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-8-methoxy-2-phenyl-4,7-methano-(2*H*)-isoindole-1,3-dione (5).[14] A solution of diene[15] (0.095 g, 0.35 mmol) and *N*-phenylmaleimide (0.093 g, 0.53 mmol) in a 10:1 mixture of CCl_4:CH_2Cl_2 (11 mL) was heated at reflux for 21 h. Yield of **5**: 0.050 g, 32%; colorless crystals. Mp: 223–224 °C. IR: 3004, 2953, 1721, 1598. ^{1}H NMR: 7.51–7.38 (3H, m), 7.14 (2H, m), 3.88 (2H, s), 3.86 (3H, s). ^{13}C NMR: 169.9, 130.8, 130.3, 129.4, 129.3, 126.4, 117.2, 77.7, 55.7, 51.7. MS: 445 (1), 443 (3), 441 (5), 439 (3) all M^+; 410 (11), 409 (8), 408 (49), 407 (16), 406 (100), 405 (13), 404 (69), 261 (30), 259 (59), 257 (46), 209 (19), 207 (20), 119 (28), 91 (16), 63 (20). HRMS: calcd for $C_{16}H_{10}{}^{35}Cl_3{}^{37}ClNO_3$ (M^+ – Cl) 405.9385, found 405.9396. Anal. Calcd for $C_{16}H_{10}Cl_5NO_3$: C, 43.53; H, 2.28; N, 3.17. Found: C, 43.56; H, 2.30; N, 3.20.

(1α,4aα,4aα,9aα,11*s*)-1,2,3,4,11-Pentachloro-1,4,4a,9a-tetrahydro-11-methoxy-1,4-methanoanthracene-9,10-dione (6).[14] A solution of diene[15] (0.063 g, 0.24 mmol) and 1,4-naphthoquinone (0.041 g, 0.26 mmol) in benzene (10 mL) was heated at reflux for 3 days. Yield of **6**: 30 mg, 29%; colorless crystals. Mp: 201–202 °C. IR: 2953, 2851, 1686, 1603. ^{1}H NMR: 8.02 (2H, m), 7.77 (2H, m), 3.92 (2H, s), 3.88 (3H, s). ^{13}C NMR: 190.1, 135.3, 134.9, 130.6, 127.2, 114.7, 80.3, 55.6, 55.1. MS: 428 (2), 426 (3) and 424 (2) all M^+; 395 (7), 394 (5), 393 (31), 392 (11), 391 (67), 390 (9), 389 (48), 261 (24), 259 (46), 257 (38), 209 (13), 207 (14), 167 (14), 104 (100), 76 (59), 50 (20). HRMS: calcd for $C_{16}H_9{}^{35}Cl_3{}^{37}ClO_3$ (M^+ – Cl) 390.9276, found 390.9264.

(3aα,4β,7β,7aα,8*s*)-4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-8-methoxy-4,7-methano-1,3-benzodioxol-2-one (7).[14] A solution of diene[15] (0.059 g, 0.22 mmol) and vinylene carbonate (0.190 g, 2.20 mmol) in toluene (1.0 mL) was heated at reflux for 8 days. The solution was concentrated under vacuum, and the brown oily residue was filtered through a plug of silica to give an orange oil, which crystallized upon standing at rt.[16] Recrystallization from ethyl acetate–hexane provided **7** as colorless crystals (0.012 g, 15%). Mp: 110–111 °C. IR: 2955, 2852, 1827, 1803, 1604. ^{1}H NMR: 5.25 (2H, s), 3.79 (3H, s). NOE data: 5.25 (3.79, 1.9%), 3.79 (5.25, 4.6%). ^{13}C NMR: 151.7, 130.2, 114.2, 83.0, 79.2, 55.8. MS: 356 (1), 354 (2) and 352 (1) all M^+; 323 (11), 322 (5), 321 (49), 320 (10), 319 (100), 318 (8), 317 (79), 268 (8), 233 (18), 231 (15), 91 (56).

(1*R,4*S**,7*R**)-1,2,3,4,7-Pentachloro-5-ethoxy-7-methoxybicyclo[2.2.1]hept-2-ene (8).** A solution of diene[15] (0.064 g, 0.24 mmol) in ethoxyethylene (8.0 mL) was heated at reflux for 3 days. Yield of **8**: 36 mg, 44%; yellow oil. IR: 3018, 2982, 2954,1610. ^{1}H NMR: 4.36 (1H, dd, J = 2.2, 7.5), 3.80 (1H, m), 3.74 (3H, s), 3.58 (1H, m), 2.70 (1H, dd, J = 7.5, 12.1), 1.90 (1H, dd, J = 2.2, 12.1), 1.16 (3H, t, J = 7.0). NOE data: 4.36 (3.74, 1.2%; 2.70, 6.5%), 2.70 (4.36, 11.7%; 3.74, 1.7%; 1.90, 21%). ^{13}C NMR: 130.9, 129.5, 115.5, 83.8, 81.3, 76.7, 67.0, 54.8, 43.5, 15.3. MS: 344 (4), 342 (13), 341 (2), 340 (19) and 338 (12) all M^+; 307 (4), 305 (9), 303 (7), 233 (26), 231 (21), 216 (19), 214 (37), 212 (100), 211 (17), 210 (100), 93 (46), 79 (59), 61 (52), 29 (72). HRMS: calcd for $C_{10}H_{11}{}^{35}Cl_4{}^{37}ClO_2$ 339.9171, found 339.9171.

(1*R,4*S**,7*R**)-1,2,3,4,7-Pentachloro-7-methoxy-5-phenylbicyclo[2.2.1]hept-2-ene (9).** A solution of diene[15] (0.093 g, 0.35 mmol) and styrene (0.035 g, 0.35 mmol) in benzene (8.0 mL) was heated at reflux for 24 h. Yield of **9**: 39 mg, 31%; pale yellow crystals. Mp: 65–67 °C. IR: 3033, 2952, 2849, 1606. ^{1}H NMR (CD_3COCD_3): 7.39–7.29 (3H, m), 7.20–7.15 (2H, m), 4.00 (1H, dd, J = 4.2, 9.1), 3.89 (3H, s), 2.94 (1H, dd, J = 9.1, 12.4), 2.52 (1H, dd, J = 4.2, 12.4). NOE data: 2.94 (4.00, 5.6%; 3.89, 2.3%; 2.52, 18%). ^{13}C NMR (CD_3COCD_3): 136.1, 131.7, 131.1, 129.8, 129.1, 128.8, 117.6, 83.6, 78.2, 55.4, 52.1, 41.4. MS: 374 (3), 372 (4) and 370 (3) all M^+; 341 (4), 340 (3), 339 (19), 338 (7), 337 (39), 336 (6), 335 (30), 299 (4), 127 (13), 125 (44), 121 (16), 104 (100). HRMS: calcd for $C_{14}H_{11}{}^{35}Cl_3{}^{37}ClO$ (M^+ – Cl) 336.9534, found 336.9518.

(1*R,4*S**,7*R**)-5-(4-Bromophenyl)-1,2,3,4,7-pentachloro-7-methoxybicyclo[2.2.1]hept-2-ene (10)**[14] **and 5-(4-Bromophenyl)-1,2,4,7,7-pentachloro-3-methoxybicyclo[2.2.1]-hept-2-ene (15).**[14] A solution of diene[15] (0.091 g, 0.34 mmol) and 4-bromostyrene (0.092 g, 0.50 mmol) in CH_2Cl_2 (8.0 mL) was heated at reflux for 20 h. Yield of **10**: 41 mg, 27%; colorless crystals. Mp: 99–100.5 °C. IR: 2995, 2951, 2850, 1605. ^{1}H NMR: 7.45 (2H, br d, J = 8.5), 6.96 (2H, br d, J = 8.5), 3.86 (3H, s), 3.81 (1H, dd, J = 4.2, 9.1), 2.83 (1H, dd, J = 9.1, 12.3), 2.34 (1H, dd, J = 4.2, 12.3). ^{13}C NMR: 134.3, 131.5, 131.0, 130.5, 130.3, 122.4, 115.9, 82.5, 77.2, 55.1, 51.2, 41.0. MS: 456 (1), 454 (5), 452 (11), 451 (1), 450 (10) and 448 (4) all M^+; 419 (19), 418 (8), 417 (49), 416 (11), 415 (58), 414 (6), 413 (26), 235 (12), 233 (21), 231 (15), 205 (35), 203 (27), 184 (97), 182 (100). HRMS: calcd for $C_{14}H_{10}{}^{79}Br{}^{35}Cl_4{}^{37}ClO$ 449.8337, found 449.8341. Anal. Calcd for $C_{14}H_{10}BrCl_5O$: C, 37.25; H, 2.23. Found: C, 37.22; H, 2.23.

Yield of the less polar adduct **15**: <2 mg; colorless crystals. Mp: 166 –168 °C. ^{1}H NMR: 7.49 (2H, br d, J = 8.5), 7.05 (2H, br d, J = 8.5), 3.86 (3H, s), 3.83 (1H, dd, J = 4.2, 9.2), 2.89 (1H, J = 9.2, 12.7), 2.44 (1H, dd, J = 4.2, 12.7). MS: 452 (2) and 450 (6) both M^+; 417 (6), 415 (6), 272 (7), 270 (25), 268 (39), 266 (25), 251 (8), 249 (35), 247 (72), 245 (58), 236 (26), 235 (34), 234 (51), 233 (68), 232 (42), 231 (49), 205 (100), 203 (79), 184 (71), 182 (71), 103 (53), 77 (61).

(1*R,4*S**,7*R**)-1,2,3,4,7-Pentachloro-7-methoxy-5-(3-nitrophenyl)bicyclo[2.2.1]hept-2-ene (11).** A solution of diene[15] (0.032 g, 0.12 mmol) and 3-nitrostyrene (0.018 g, 0.12 mmol) in benzene (10 mL) was heated at reflux for 5 days. Yield of **11**: 19 mg, 38%; yellow solid. Mp: 106–108 °C. IR: 2954, 2851, 1605, 1532. ^{1}H NMR (CD_3COCD_3): 8.24 (1H, dt, J = 7.1, 2.1), 8.10 (1H, nar m), 7.74–7.65 (2H, m), 4.27 (1H, dd, J = 4.2, 9.1), 3.92 (3H, s), 3.05 (1H, dd, J = 9.1, 12.6), 2.67 (1H, dd, J = 4.2, 12.6). NOE data: 3.92 (4.27, 3.0%; 3.05, 1.7%), 3.05 (4.27, 12%; 3.92, 0.9%; 2.67, 18%). ^{13}C NMR (CD_3COCD_3): 149.0, 138.7, 136.2, 132.6, 130.7, 130.6, 124.7, 123.8, 117.4, 83.4, 78.2, 55.6, 51.7, 41.4. MS: 419 (0.4), 417 (0.9) and 415 (0.4) all M^+; 388 (1), 387 (2), 386 (11), 385 (8), 384 (49), 383 (17), 382 (100), 381 (15), 380 (77), 270 (8), 268 (12), 266 (7), 233 (29), 231 (22), 170 (29). HRMS: calcd for $C_{14}H_{10}{}^{35}Cl_3{}^{37}ClNO_3$ (M^+ – Cl) 381.9385, found 381.9407.

(1*R,4*S**,7*R**)-1,2,3,4,7-Pentachloro-7-methoxy-5-(2-naphthyl)bicyclo[2.2.1]hept-2-ene (12).** A solution of diene[15] (0.034 g, 0.13 mmol) and 2-vinylnaphthalene (0.021 g, 0.14 mmol) in benzene (10 mL) was heated at reflux for 4 days. Yield of **12**: 14 mg, 26%; oil, which slowly crystallized in the refrigerator. Mp: 104–106 °C. IR: 3058, 3021, 2952, 2849, 1606. ^{1}H NMR: 7.84–7.78 (3H, m), 7.56 (1H, br d, J = 1.5), 7.49 (2H, symmetrical m), 7.20 (1H, dd, J = 1.9, 7.6), 4.03 (1H, dd, J = 4.2, 9.1), 3.90 (3H, s), 2.91 (1H, dd, J = 9.1, 12.3), 2.54

(14) Atomic coordinates for the X-ray structures of **5–7**, **10**, **13–15** have been deposited with the Cambridge Crystallographic Data Centre. These coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, U.K.

(15) The diene used in these experiments was a 1.5:1 mixture of **1** and **4**. Yields were calculated as if the diene were pure **1** because one could not be sure if **1** and **4** were interconverting at the reaction temperature. Nevertheless, in most instances some **4** was evident, unreacted, at the termination of the reaction. This may in part explain the low yields calculated for the adducts.

(16) Attempts to purify **7** by flash column chromatography led to decomposition.

(1H, dd, J = 4.2, 12.3). NOE data: 4.03 (7.56, 8.8%; 7.20, 6.7%; 3.90, 0.3%; 2.91, 6.9%), 3.90 (4.03, 1.7%; 2.91, 1.4%), 2.91 (4.03, 9.2%; 3.90, 1.1%; 2.54, 14%). ^{13}C NMR: 133.0, 132.9, 132.7, 128.5, 128.1, 128.0, 127.6, 126.4, 126.3 (2C), 116.2, 82.8, 77.2, 55.1, 51.8, 41.3. MS: 426 (1), 424 (4), 423 (1), 422 (6) and 420 (4) all M^+; 389 (3), 387 (5), 385 (4), 236 (4), 175 (20), 171 (12), 154 (100), 153 (12). HRMS: calcd for $C_{18}H_{13}{}^{35}Cl_3{}^{37}ClO$ (M^+ − Cl) 386.9690, found 386.9686.

(1*R*,4*S*,10*S*)-5,6,7,8,10-Pentachloro-5,8-dihydro-10-methoxy-2-phenyl-5,8-methano-(1*H*)-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (13).[14] A solution of diene[15] (0.063 g, 0.15 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (0.053 g, 0.30 mmol) in benzene (7.0 mL) was heated at 75 °C overnight. Yield of **13**: 0.036 g, 55%; colorless crystals. Mp: 99−101 °C. IR: 2957, 2854, 1802, 1750, 1582. ^{1}H NMR: 7.52−7.40 (3H, m), 7.38−7.34 (2H, m), 3.93 (3H, s). ^{13}C NMR: 155.4, 129.7, 129.5, 128.6, 125.5, 109.5, 90.5, 56.0. MS: 447 (2), 445 (6), 443 (9) and 441 (5) all M^+; 412 (11), 411 (8), 410 (48), 409 (16), 408 (100), 407 (13), 406 (77), 299 (17), 289 (34), 287 (27), 270 (23), 268 (36), 266 (23), 263 (12), 261 (24), 259 (19), 235 (33), 233 (67), 231 (51), 218 (20), 216 (16), 119 (84), 91 (35), 64 (21), 63 (29). HRMS: calcd for $C_{14}H_8{}^{35}Cl_3{}^{37}ClN_3O_3$ (M^+ − Cl) 407.9289, found 407.9284. Anal. Calcd for $C_{14}H_8Cl_5N_3O_3$: C, 37.92; H, 1.82; N, 9.47. Found: C, 38.06; H, 1.95; N, 9.35.

(1*R*,4*S*,7*s*)-1,2,3,4,7-Pentachloro-5,6-bis(ethyloxycarbonyl)-7-methoxybicyclo[2.2.1]hepta-2,5-diene (14).[14] A solution of diene[15] (0.117 g, 0.437 mmol) and diethyl acetylenedicarboxylate (0.272 g, 1.60 mmol) in benzene (10 mL) was heated at reflux for 10 days. Yield of **14**: 81 mg, 42%; colorless crystals. Mp: 62−64 °C. IR: 2986, 2954, 2907, 2851, 1731, 1629, 1603. ^{1}H NMR: 4.32 (4H, complex symmetrical m), 3.77 (3H, s), 1.34 (6H, t, J = 7.1). ^{13}C NMR: 160.7, 143.3, 137.5, 128.8, 81.2, 62.4, 56.4, 14.0. MS: no M^+; 407 (2), 406 (1), 405 (8), 404 (3), 403 (16), 402 (2) and 401 (12) all M^+ − Cl; 331 (50), 329 (100), 327 (79), 279 (61), 277 (60), 207 (13), 205 (13), 29 (84). HRMS: calcd for $C_{14}H_{13}{}^{35}Cl_3{}^{37}ClO_5$ (M^+ − Cl) 402.9487, found 402.9469. Anal. Calcd for $C_{14}H_{13}Cl_5O_5$: C, 38.35; H, 2.99. Found: C, 38.62; H, 3.09.

Acknowledgment. We thank Mr. C. C. Pye for the ab initio calculations. We are grateful to Ms. S. Gillingham for assistance with the X-ray crystallography on two adducts. This work was supported from a research grant from the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: X-ray structures for **5−7**, **10**, and **13−15**, ^{1}H NMR spectra of **5−15**, ^{13}C NMR spectra of **5−14**, and a table of ^{13}C NMR data for some adducts of **1−3** (30 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.

JO950776W