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Stereoselectivities of Diels-Alder Cycloadditions of Tricyclic Dienes to MTAD, PTAD, and *N*-Methylmaleimide

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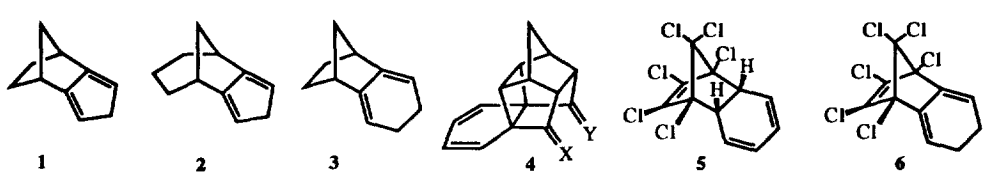
Abstract: Diels-Alder cycloadditions of 1,2,3,4,9,9-hexachloro-1α,4α,4aα,8aβ-tetrahydro-1,4-methanonaphthalene (**5**) and 1,2,3,4,9,9-hexachloro-1α,4α,6,7-tetrahydro-1,4-methanonaphthalene (**6**) to 4-methyl- and 4-phenyl-1,2,4-triazoline-3,5-dione [MTAD and PTAD, respectively] and to *N*-methylmaleimide (NMM) have been studied. The structures of several of the resulting cycloadducts were determined unequivocally by X-ray crystallographic methods. © 1997 Elsevier Science Ltd.

INTRODUCTION

Stereoselectivities of Diels-Alder cycloadditions of various dienophiles to facially differentiated dienes comprise a topic of intense current interest. Recent examples in this regard include "isodicyclopentadiene" (**1**),[1] unsymmetrically annulated diene **2**,[2] and unsymmetrically annulated cyclohexa-1,3-dienes **3**[3] and **4**[4] (Scheme 1).

In order to gain further insight into the steric and electronic factors that control [4 + 2] cycloadditions between facially dissymmetric dienes and highly reactive dienophiles, studies of Diels-Alder cycloadditions of two isomeric annulated cyclohexadienes, i. e., **5** and **6**, to 4-methyl- and 4-phenyl-1,2,4-triazoline-3,5-dione [MTAD and PTAD, respectively] were undertaken. In addition, the corresponding Diels-Alder cycloaddition of **5** to *N*-methylmaleimide (NMM) was studied.

Scheme 1

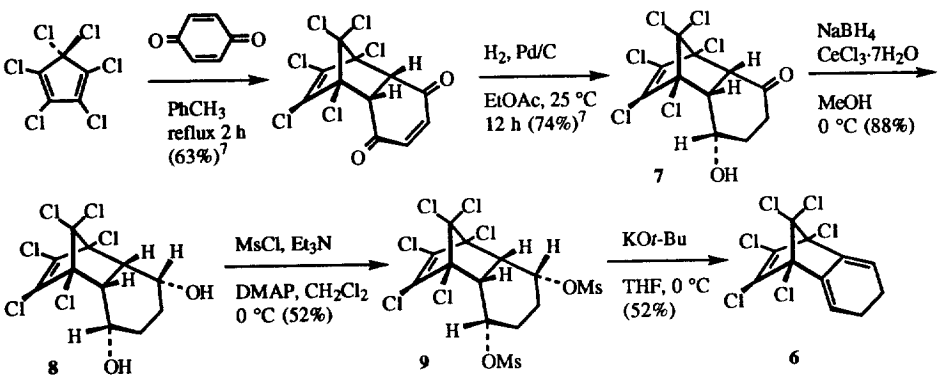


1 **2** **3** **4** **5** **6**

RESULTS AND DISCUSSION

Preparation of Dienes 5 and 6. The synthesis of diene **5** has been reported previously.[5] Diene **6** was prepared by using the method shown in Scheme 2. Thus, $NaBH_4$-$CeCl_3$ promoted reduction[6] of **7**[7] afforded the corresponding diol, **8** (88% yield), which subsequently was converted into the corresponding dimesylate and thence to the target diene, **6**.

Scheme 2

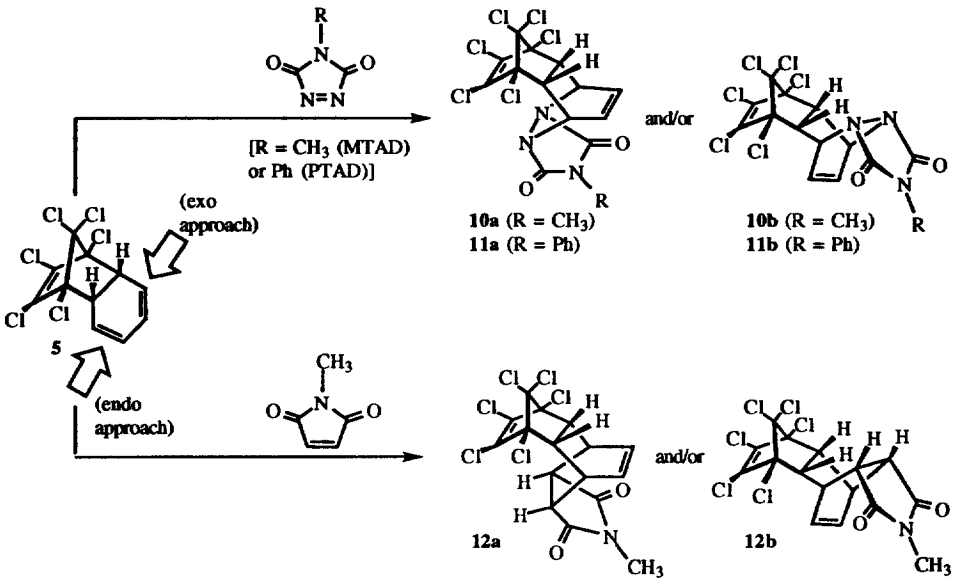


Diels-Alder Cycloadditions of Dienes 5 and 6. In each case, either (or both) of two [4 + 2] cycloadducts can possibly result via Diels-Alder cycloadditions of diene **5** to MTAD, PTAD, and/or NMM (Scheme 3). In our hands, cycloaddition of **5** to all three reactive dienophiles occurred with exclusive attack of the dienophile upon the *exo* face of the diene, thereby producing a single cycloadduct in each case (i. e., **10b**, **11b**, and **12b**, respectively, Scheme 3). The stereochemistry of each of these Diels-Alder cycloadditions was established unequivocally via subsequent facile intramolecular [2 + 2] photocyclization of **10b**, **11b**, and **12b** to the corresponding polycarbocyclic "cage" structure, (i. e., **13**, **14**, and **15**, respectively, Scheme 4).

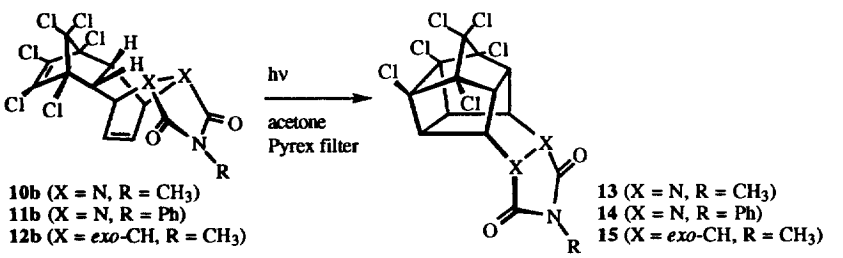
Thermal Diels-Alder cycloadditions of **6** to MTAD and to PTAD both occurred significantly more slowly than the corresponding reactions of diene **5** with these same two dienophiles. Thus, [4 + 2] cycloaddition of **6** to MTAD afforded two isomeric cycloadducts, **16a** and **16b** (product ratio: 4.3 : 1, Scheme 5). The structure of the major product, **16a**, was established unequivocally by application of direct methods (i. e., single crystal X-ray structural analysis; see the Experimental Section). Similarly, [4 + 2] cycloaddition of **6** to PTAD again afforded two isomeric cycloadducts, **17a** and **17b** (product ratio: 4.8 : 1). Once again, the structure of the major product, **17a**, was established unequivocally via application of X-ray crystallographic methods.

Diels-Alder cycloaddition of **5** to NMM occured much more slowly than did the corresponding [4 + 2] cycloadditions of **5** to MTAD and/or PTAD. Interestingly, **6** could not be induced to undergo Diels-Alder cycloaddition to NMM, even when a benzene solution of the two reactants was refluxed for 7 days.

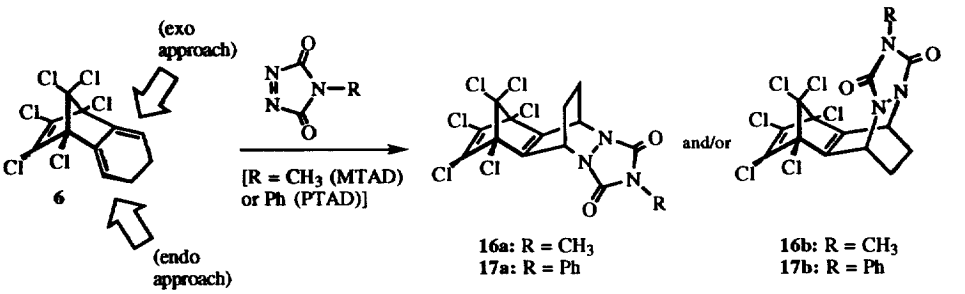
Scheme 3



Scheme 4



Scheme 5



SUMMARY AND CONCLUSIONS

Diels-Alder reactions of hexachlorodienes **5** and **6** with a variety of dienophiles (i. e., MTAD, PTAD, and NMM) have been performed, and the structures of the resulting cycloadducts have been established. Diels-Alder cycloadditions of **5** to MTAD, PTAD and NMM all proceed via exclusive approach of the dienophile toward the *exo* π-face of the diene. By way of contrast, the corresponding reactions of **6** with MTAD and PTAD in each case afford a mixture of two isomeric [4 + 2] cycloadducts wherein the major product results via approach of the dienophile to the *endo* π-face of the diene. Diene **6** is unreactive toward NMM (conditions: benzene solvent, reflux 7 days). The structures of the various [4 + 2] cycloadducts were established unequivocally either via (i) intramolecular [2 + 2] photocyclization to the corresponding cage structure or (ii) application of X-ray crystallographic methods.

EXPERIMENTAL SECTION

Melting points are uncorrected. Elemental microanalyses were performed by personnel at M-H-W Laboratories, Phoenix, AZ.

1,2,3,4,9,9-Hexachloro-1α,4α,4aα,5α,6,7,8β,8aα-octahydro-1,4-methanonaphthalene-5,8-diol (8).[6] A solution of **7**[7] (2.83 g, 7.36 mmol) and $CeCl_3 \cdot 7H_2O$ (3.20 g, 8.59 mmol) in CH_3OH (30 mL) was cooled to *ca.* 0 °C via application of an external ice-water bath. To this cooled solution, solid $NaBH_4$ (1.00 g, 26.4 mmol, excess) was added portionwise with stirring in such a manner that the temperature of the reaction mixture did not exceed 5 °C. The resulting mixture was stirred at 0-5 °C for 4 h, at which time the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature. Thin layer chromatographic (tlc) analysis of the reaction mixture revealed the absence of **7**. The reaction mixture was concentrated *in vacuo*, thereby affording a pale yellow solid residue. To this residue was added 10% aqueous HCl (20 mL), and the resulting aqueous suspension was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed sequentially with saturated aqueous $NaHCO_3$ (2 x 10 mL) and water (2 x 10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Crude **8** (2.49 g, 88%) was thereby obtained; repeated recrystallization of this material from CH_2Cl_2 afforded pure **8** as a colorless microcrystalline solid: mp 204-205 °C (dec.); IR (KBr) 3200 (br, m), 2935 (w), 1607 (m), 1001 (m), 874 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.67-2.07 (m, 4 H), 2.88 (t, J = 1.7 Hz, 2 H), 3.45 (br s, 2 H), 4.33 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.1 (t), 50.6 (d), 62.6 (d), 80.9 (s), 104.6 (s), 131.6 (s). Anal. Calcd for $C_{11}H_{10}Cl_6O_2$: C, 34.15; H, 2.61. Found: C, 34.34; H, 2.66.

1,2,3,4,9,9-Hexachloro-1α,4α,4aα,5α,6,7,8β,8aα-octahydro-1,4-methanonaphthalene-5,8-dimesylate (9). To a solution of **8** (2.49 g, 6.44 mmol) in CH_2Cl_2 (40 mL) was added Et_3N (3.04 g, 30 mmol, excess) and 4-dimethylaminopyridine (DMAP, 890 mg, 7.30 mmol), and the resulting solution was cooled to *ca.* 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring MsCl (1.34 mL, 17.2 mmol). After the addition of MsCl had been completed, the reaction mixture was stirred at 0-5 °C for 4 h, at which time the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture was filtered, and the residue, a yellow-orange solid, was washed sequentially with ice-cold CH_2Cl_2 (3 x 10 mL) and water (2 x 10 mL). Crude **9** (1.81 g, 52%) was thereby obtained as a colorless solid. Repeated recrystallization of this material from CH_2Cl_2 afforded pure **9** as colorless flakes: mp 207-208 °C; IR (KBr) 3025 (w), 2928 (w), 1362 (m), 1337 (s), 1173 (s), 1061 (m), 843 (m) 862 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.92 (m, 2 H), 2.46 (m, 2 H), 3.10 (s, 6 H), 3.31 (dd, J = 1.9, 3.3 Hz, 2 H), 5.18 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.0 (t), 38.6 (q), 48.6 (d), 70.5 (d), 79.8 (s), 105.6 (s), 132.3 (s). Anal. Calcd for $C_{11}H_{10}Cl_6O_2$: C, 28.75; H, 2.60. Found: C, 28.64; H, 2.47.

1,2,3,4,9,9-Hexachloro-1α,4α,6,7-tetrahydro-1,4-methanonaphthalene (6). A solution of **9** (600 mg, 1.10 mmol) in dry THF (30 mL) under argon was cooled to *ca.* 0 °C via application of an external ice-water bath and then was stirred for 0.5 h. To this cooled solution was added KOt-Bu (265 mg, 2.36 mmol), and the resulting mixture was stirred for 1 h. The reaction was quenched via addition of CH_3OH (10 mL), and the resulting mixture was concentrated *in vacuo*. To the residue thereby obtained were added water (20 mL) and hexane (30 mL), and the layers were separated. The aqueous layer was extracted with hexane (3 x 20 mL). The combined organic layers were washed with water (2 x 5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo* to afford crude **6** (211 mg, 52%). Column chromatographic purification of this material on silica gel by eluting with hexane afforded pure **6** as a colorless microcrystalline solid: mp 85-86 °C; IR (KBr) 3074 (w), 2943 (m), 2832 (w), 1595 (s), 1149 (s), 1005 (m), 909 (s), 799 (m), 687 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.40 (s, 4 H); 5.95 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.3 (t), 82.3 (s), 104.4 (s), 120.0 (d), 131.8 (s), 132.0 (s). Anal. Calcd for $C_{11}H_6Cl_6$: C, 37.65; H, 1.72. Found: C, 37.75; H, 1.83.

Diels-Alder Cycloaddition of 5 to 4-Methyl-1,2,4-triazoline-3,5-dione (MTAD). A solution of **5**[5] (500 mg, 1.42 mmol) and MTAD (161 mg, 1.42 mmol) in dry benzene (20 mL) under argon was refluxed for 4 h, at which time tlc analysis indicated the absence of **5**. The reaction mixture was concentrated *in vacuo*, and the residue was recrystallized from EtOAc-hexane. Pure **10b** (520 mg, 80%) was thereby obtained as a colorless microcrystalline solid: mp 247-248 °C; IR (KBr) 3000 (w) 2939 (w), 1788 (m), 1720 (s), 1606 (s), 1459 (m), 1394 (s), 1269 (w), 1186 (w), 1035 (w), 756 (m), 692 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 2.99 (s, 3 H), 3.45 (s, 2 H), 5.01-5.03 (m, 2 H), 6.22-6.26 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.1 (q), 47.4 (d), 51.0 (d), 79.8 (s), 104.2 (s), 125.9 (d), 130.2 (s), 158.1 (s). Anal. Calcd for $C_{14}H_9Cl_6N_3O_2$: C, 36.24; H, 1.95. Found: C, 36.56; H, 1.89.

Intramolecular Photocyclization of 10b. A solution of **10b** (100 mg, 0.22 mmol) in acetone (500 mL) was irradiated with a Hanovia 450 W medium pressure Hg immersion lamp (Pyrex filter) for 4 h, at which time tlc analysis indicated the absence of **10b**. The reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 1:7 EtOAc-hexane. Pure **13** (65 mg, 65%) was thereby obtained as a colorless microcrystalline solid: mp 273-274 °C; IR (KBr) 2997 (m), 1776 (s), 1721 (s), 1512 (s), 1473 (m), 1394 (w), 1260 (s), 1160 (s), 1000 (s), 910 (s), 732 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 3.03 (s, 3 H), 3.20-3.50 (m, 4 H), 5.00-5.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.1 (q), 46.3 (d), 50.3 (d), 50.6 (d), 76.4 (s), 80.7 (s), 94.0 (s), 153.9 (s). Anal. Calcd for $C_{14}H_9Cl_6N_3O_2$: C, 36.24; H, 1.95. Found: C, 36.37; H, 2.04.

Diels-Alder Cycloaddition of 5 to 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD). A solution of **5**[5] (44 mg, 0.13 mmol) and PTAD (34 mg, 0.19 mmol) in dry benzene (10 mL) under argon was refluxed for 4 h, at which time tlc analysis indicated the absence of **5**. The reaction mixture was concentrated *in vacuo*. The residue, a pink solid, was purified via fractional recrystallization from CH_2Cl_2-hexane mixed solvent. Pure **11b** (59 mg, 89%), was thereby obtained as a colorless microcrystalline solid: mp 247-248 °C; IR (KBr) 2920 (w), 2847 (w), 1787 (m), 1723 (s), 1413 (s), 1062 (w), 683 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 3.51 (br s, 2 H), 5.13 (m, 2 H), 6.34 (t, J = 3.7 Hz, 2 H), 7.3-7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 46.9 (d), 50.7 (d), 79.3 (s), 103.7 (s), 125.4 (d), 125.7 (d), 128.7 (d), 129.3 (d), 129.8 (s), 130.8 (s), 156.0 (s). Anal. Calcd for $C_{19}H_{11}Cl_6N_3O_2$: C, 43.38; H, 2.11. Found: C, 43.50; H, 2.17.

Intramolecular Photocyclization of 11b. A solution of **11b** (40 mg, 0.076 mmol) in acetone (150 mL) was irradiated for 6 h with a Hanovia 450 W medium pressure Hg immersion lamp which had been fitted with a Pyrex filter. At the conclusion of the reaction, the reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 12% EtOAc-hexane. Pure **14** (22 mg, 55%) was thereby obtained as a colorless microcrystalline solid: mp 262-263 °C; IR (KBr) 2928 (m), 2866 (w), 1769 (s), 1714 (s), 1504 (m), 1414 (s), 1283 (m), 1012 (m), 872 (m), 758 (s), 639 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 3.37 (t, J = 2.2 Hz, 2 H), 3.41 (d, J = 1.9 Hz, 2 H), 5.11 (q, J = 2.1 Hz, 2 H), 7.33-7.53 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 46.0 (d), 50.1 (d), 50.4 (d), 76.0 (s), 80.2 (s), 93.8 (s), 125.3 (d), 128.6 (d), 129.3 (d), 130.9 (s), 151.3 (s). Anal. Calcd for $C_{19}H_{11}Cl_6N_3O_2$: C, 43.38; H, 2.11. Found: C, 43.56; H, 2.12.

Diels-Alder Cycloaddition of 5 to *N*-Methylmaleimide. A solution of diene **5**[5] (60 mg, 0.17 mmol) and *N*-methylmaleimide (40 mg, 0.36 mmol) in dry benzene (25 mL) under argon was refluxed for 40 h. The reaction mixture was concentrated *in vacuo*, and the residue was recrystallized from CH_2Cl_2-hexane mixed solvent. Pure **12b** (47 mg, 64%) was thereby obtained as a colorless microcrystalline solid: mp 268-269 °C; IR (KBr) 2923 (w), 2858 (w), 1701 (s), 1433 (w), 1369 (w), 1286 (w), 1047 (w), 684 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.76 (s, 3 H), 2.81 (t, J = 1.4 Hz, 2 H), 2.84 (s, 2 H), 3.33 (br s, 2 H), 5.86 (dd, J = 4.4, 3.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.8 (q), 31.6 (d), 44.8 (d), 49.5 (d), 80.5 (s), 103.8 (s), 127.3 (d), 129.8 (s), 176.4 (s). Anal. Calcd for $C_{16}H_{11}Cl_6NO_2$: C, 41.60; H, 2.40. Found: C, 41.78; H, 2.38.

Intramolecular [2 + 2] Photocyclization of 12b. A solution of **12b** (47 mg, 0.10 mmol) in acetone (150 mL) was irradiated for 15 h with a Hanovia 450 W medium pressure Hg immersion lamp which had been fitted with a Pyrex filter. At the conclusion of the reaction, the reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 20% EtOAc-hexane. Pure **15** (12 mg, 25%) was thereby obtained as a colorless microcrystalline solid: mp 273-274 °C; IR (KBr) 2933 (w), 2847 (w), 1705 (s), 1429 (m), 1379 (m), 1282 (m), 1118 (w), 1022 (w), 749 (m), 684 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.99-3.14 (m, 6 H), 2.98 (s, 3 H), 2.79 (q, J = 2.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.1 (q), 31.8 (d), 36.3 (d), 45.0 (d), 51.1 (d), 78.3 (s), 82.3 (s), 93.7 (s), 176.9 (s). Anal. Calcd for $C_{16}H_{11}Cl_6NO_2$: C, 41.60; H, 2.40. Found: C, 41.48; H, 2.34.

Diels-Alder Cycloaddition of 6 to 4-Methyl-1,2,4-triazoline-3,5-dione (MTAD). A solution of **6** (165 mg, 0.46 mmol) and MTAD (90 mg, 0.75 mmol) in dry benzene (25 mL) under argon was refluxed for 16 h. The reaction mixture was concentrated *in vacuo*. The proton NMR spectrum of the residue thereby obtained revealed the presence of two isomeric [4 + 2] cycloadducts (i. e., **16a** and **16b**, product ratio **16a**:**16b** = 4.3 : 1). The residue was recrystallized from CH_2Cl_2-hexane mixed solvent. Pure **16a** (major product, 96 mg, 44%) was thereby obtained as a colorless microcrystalline solid: mp 207-208 °C; IR (KBr) 2952 (w), 2930 (w), 2851 (w), 1788 (m), 1722 (s), 1458 (m), 1400 (m), 1282 (w), 1186 (w), 1120 (w), 1060 (w), 1020 (w), 904 (w), 696 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.67 (m, 2 H), 2.27 (m, 2 H), 2.88 (s, 3 H), 5.18 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.5 (t), 25.4 (q), 51.0 (d), 83.8 (s), 116.8 (s), 138.1 (s), 144.4 (s), 158.2 (s). Anal. Calcd for $C_{14}H_9Cl_6N_3O_2$: C, 36.24; H, 1.95. Found: C, 36.41; H, 2.08. The structure of **16a** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

The mother liquor which remained after pure **16a** had been isolated by fractional recrystallization was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 12% EtOAc-hexane. An additional quantity of pure **16a** (80 mg, 36%; total yield of **16a** collected: 176 mg, 80%) was thereby obtained. Continued elution of the chromatography column with 15% EtOAc-hexane afforded pure **16b** (18 mg, 8%) as a colorless microcrystalline solid: mp 220-221 °C; IR (KBr) 3007 (w), 2959 (w), 2373 (w), 2343 (w), 1786 (m), 1732 (s), 1448 (m), 1391 (m), 1196 (m), 1125 (m), 907 (m), 783 (m), 710 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.30 (*AB*, J_{AB} = 9.6 Hz, 2 H), 1.35 (A*B*, J_{AB} = 9.6 Hz, 2 H), 2.88 (s, 3 H), 5.23 (t, J = 1.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.8 (t), 25.3 (q), 49.1 (d), 83.1 (s), 117.9 (s), 138.7 (s), 146.7 (s), 157.2 (s). Anal. Calcd for $C_{14}H_9Cl_6N_3O_2$: C, 36.24; H, 1.95. Found: C, 36.44; H, 2.21. The structure of **16b** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

Diels-Alder Cycloaddition of 6 to 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD). A solution of **6** (50 mg, 0.14 mmol) and PTAD (25 mg, 0.14 mmol) in dry toluene (15 mL) under argon was refluxed for 2 h. The reaction mixture was concentrated *in vacuo*. The proton NMR spectrum of the residue thereby obtained revealed the presence of two isomeric [4 + 2] cycloadducts (i. e., **17a** and **17b**, product ratio **17a**:**17b** = 4.8 : 1). Fractional recrystallization of this material from EtOAc-hexane mixed solvent afforded the major reaction product, pure **17a** (42 mg, 56%) as a colorless microcrystalline solid: mp 229-230 °C; IR (KBr) 2920 (w), 2847 (w), 1776 (m), 1722 (s), 1496 (m), 1232 (m), 1150 (w) 1113 (m), 1057 (w), 689 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.73 (*AB*, J_{AB} = 9.5 Hz, 2 H), 2.35 (A*B*, J_{AB} = 9.5 Hz, 2 H), 5.31 (t, J = 1.3 Hz, 2 H), 7.27-7.47 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.8 (t), 50.5 (d), 84.0 (s), 117.3 (s), 125.5 (d), 128.6 (d), 129.2 (d), 130.6 (s), 138.1 (s), 145.1

(s), 156.1 (s). Anal. Calcd for $C_{19}H_{11}Cl_6N_3O_2$: C, 43.38; H, 2.11. Found: C, 43.40; H, 2.10. The structure of **17a** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

X-ray Crystal Structures of 16a, 16b, and 17a. All data were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω–2θ scan technique, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[8] Pertinent X-ray data are given in Table 4. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (**16a** and **17a** were solved by using SIR[9], while **16b**, was solved by using SHELXS-86[10]), and the model was refined by using full-matrix least-squares techniques. All non-hydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms were located on difference maps and then were included in the model in idealized positions [U(H) = 1.3 B_{eq}(C)] wherever possible. All computations other than those specified were performed by using MolEN.[11] Scattering factors were taken from the usual sources.[12]

Table 4. X-ray data collection and processing parameters for **16a**, **16b**, and **17a**.

Compound	16a	16b	17a
	$C_{14}H_9Cl_6N_3O_2$	$C_{14}H_9Cl_6N_3O_2$	$C_{19}H_{11}Cl_6N_3O_2$
Size (mm)	0.3 x 0.3 x 0.2	0.08 x 0.10 x 0.42	0.42 x 0.52 x 0.58
Space Group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	8.4265 (6)	10.796 (1)	15.966 (1)
b (Å)	26.460 (2)	12.823 (2)	8.3787 (6)
c (Å)	8.5180 (7)	12.884 (3)	15.7600 (8)
β (°)	110.518 (1)	92.40 (1)	101.465 (5)
V (Å^3)	1778.7 (3)	1782.1 (1)	2066.2 (2)
Z-value	4	4	4
D_{calc} (g-cm^{-3})	1.732	1.729	1.691
μ (cm^{-1})	9.86	9.84	8.59
T (K)	295	223	295
$2\theta_{max}$ (°)	50	44	44
Total reflections	3393	2436	2819
Unique reflections	3179	2305	2720
R_{int}	0.024	0.016	0.020
$I \geq 3\sigma(I)$	2644	1756	2037
Parameters	226	226	271
R, R_w	0.0566, 0.0654	0.0291, 0.0290	0.0276, 0.0511
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01	< 0.01
ρ_{max}; ρ_{min} (eÅ^{-3})	0.44; -0.35	0.22; -0.21	0.27; -0.27

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