Benzoannulation of Quinones by a Cycloaddition-Fragmentation Approach. A Simple Synthesis of Methoxycarbonyl-Substituted Polyacenoquinones

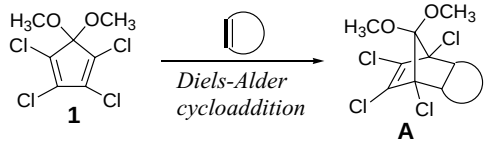
Teh-Chang Chou* (周德璋), Chia-Jung Hsu (許家融) and Jao-Yu Chen (陳昭妤)
Department of Chemistry and Biochemistry, National Chung Cheng University, Ming Hsiung, Chia Yi 621, Taiwan, R.O.C.

The cycloadducts **2A**-**5A** obtained from the Diels-Alder cycloadditions of 1,2,3,4-tetrachloro-4,5-dimethoxycyclopentadiene (**1**) with *p*-benzoquinone (**2**), 1,4-naphthoquinone (**3**), 1,4-anthraquinone (**4**), and 2,3-dicyano-1,4-benzoquinone (**5**) were subjected to the reaction with triethylamine in dichloromethane at room temperature. Cycloadducts **2A** and **5A** enolized to give the corresponding hydroquinones **2B** and **5B**, which were oxidized with DDQ to afford naphthoquinone ester **2D** and anthraquinone ester **5D**, respectively. In the cases of cycloadducts **3A** and **4A**, the enolization occurred concurrently with oxidation and fragmentation to produce directly the polyacenoquinone esters **3D** and **4D**, respectively. Under the same reaction condition, the unsymmetrical cycloadduct **6A** derived from naphthoquinone ester **2D** and **1** yielded isomeric polyacenoquinone esters **6Da** and **6Db** in a ratio of about 8:1.

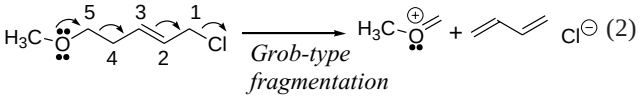
Keywords: Benzoannulation; Polyacenoquinones; Diels-Alder reactions; Grob fragmentation.

INTRODUCTION

Ever since its preparation was first reported by Newcomer and McBee in 1949,[1] 1,2,3,4-tetrachloro-4,5-dimethoxycyclopentadiene (**1**) has been extensively utilized as a cyclic diene in the Diels-Alder cycloadditions with a wide range of dienophiles.[2] This electron deficient cyclic diene **1** reacts successfully with dienophiles having both electron deficient and electron rich groups under mild conditions and generally provides excellent yields of cycloadducts with a high degree of stereoselectivity (eq. 1). The Diels-Alder cycloadducts **A** thereby formed possess 1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2.2.1]heptene ring skeleton and constitute important building blocks for the synthesis of diverse complex non-natural[3] as well as natural products.[4] The ring skeleton contains an electrofugal group (CH_3O-C-) and a nucleofugal atom (-Cl), which are intercalated by a but-2-en-1,4-diyl (-C-C=C-C-) fragment. This combination creates a setting for the event of Grob-type fragmentation[5] (eq. 2) to occur that is relayed by the C2-C3 double bond and driven by the relief of ring strain. The fragmentation would occur much more readily in the reactions of the corresponding tetrachloroketones, which are derived from the cycloadducts **A** by deketalization, and a nucleophile, such as hydroxide and alkoxides,[6] and could be further facilitated by the electron-withdrawing substituents at ring-junction carbon atoms and the eventual aromatization. This intrinsic feature offers additional application of cycloadducts **A** to the synthesis of chlorinated aromatic acids and esters.[7]



(1)

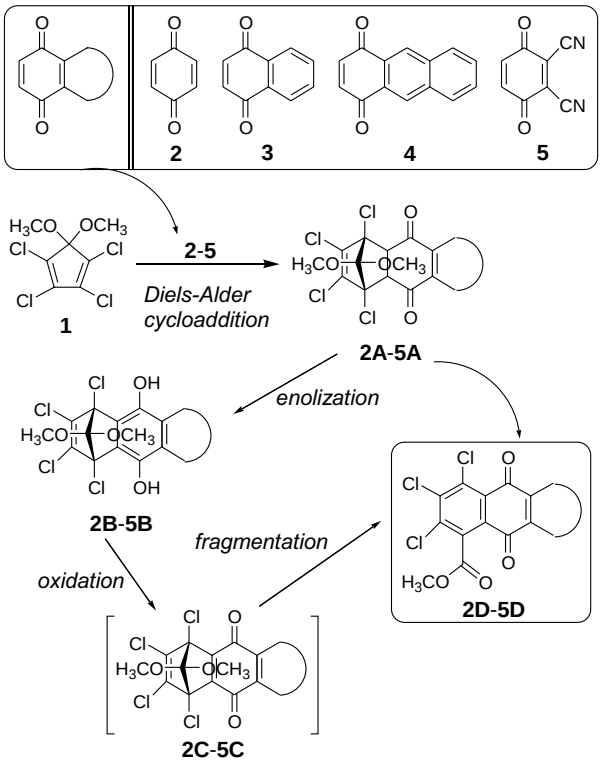


(2)

As part of a current research program that is aimed at the design and synthesis of photochromic molecules, it was necessary for us to search for the derivatives of polyacenequinones and polyacenes. In this context, we undertook a study on the accessibility of an approach that was based on a combination of Diels-Alder cycloaddition and fragmentation reaction using cyclic diene **1** and quinone dienophiles, as outlined in Scheme I. It has been shown that the Diels-Alder cycloadduct of cyclic diene **1** and dimethyl acetylenedicarboxylate undergoes thermal fragmentation to produce tri-

* Corresponding author. Fax: +886-5-2721040; e-mail: chetcc@ccu.edu.tw

Scheme I



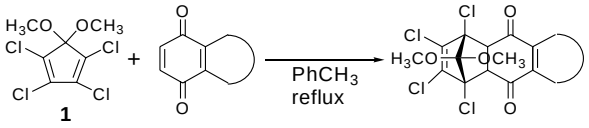
methyl 4,5,6-trichlorobenzene-1,2,3-tricarboxylate and chloromethane below the temperature (110 °C) required for its formation.[8] We thus envisioned that once the annulated 1,4-quinones **2C**-**5C** were formed by the oxidation of hydroquinones **2B**-**5B**, they would likely undergo rapid fragmentation to afford polyacenoquinones **2D**-**5D**. The overall conversion to polyacenoquinone esters shown by Scheme I was first described by Kniel on the bromination reaction of cycloadduct **3A** to yield directly the fragmented anthraquinone ester **3D**,[9a] which could also be obtained by the thermolysis of **3A** at 240 °C followed by the oxidation with CrO_3.[9b] More recently Mehta[10a] and Marchand[10b] reported that the enolization of cycloadduct **2A** to hydroquinone **2B** followed by a CAN-promoted oxidation of **2B** did not furnish the corresponding annulated 1,4-benzoquinone **2C**. Instead, fragmentation occurred with concomitant aromatization to afford naphthoquinone ester **2D**. In this paper, we report our results of preparing the polyacenoquinone derivatives **2D**-**5D** by benzoannulation of 1,4-quinones **2**-**5** based on a Diels-Alder cycloaddition-fragmentation approach using cyclic diene **1** as benzoannulating agent (Scheme I). In most cases, the preparation consists of only two operations with a mild reaction condition for the one-pot, tandem enolization-oxidation-fragmentation (**2A**-**5A**→**2D**-**5D**) using triethylamine to promote enolization and air as the oxidant supplier. The study was extended to the unsymmetrical cycloadduct **6A**, which was made available from the Diels-Alder cycloaddition of **2D** with cyclic diene **1**. The triethylamine-promoted fragmentation reaction of **6A** was found to yield **6Da**/**6Db** directly and displayed significant regioselectivity. The result is also reported herein.

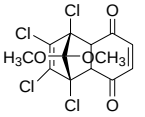
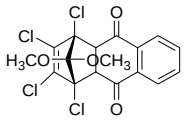
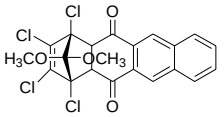
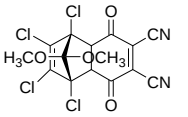
RESULTS AND DISCUSSION

Following the established procedure with modification,[11] the preparation of Diels-Alder cycloadducts of cyclic diene **1** and the 1,4-quinone dienophiles **2**-**5** was performed in toluene at refluxing temperature, and the results are summarized in Table 1. The structures of cycloadducts **2A** and **3A** were assured by comparison of ^{1}H NMR spectral data with the reported ones,[10] and those of **4A** and **5A** by the spectral and elemental analyses. Since the stereochemistry of the Diels-Alder cycloadducts **2A** and **3A** has been established to have *endo*-configuration in accordance with the Alder-rule by converting to the corresponding cage compounds using a photochemical [2+2]cycloaddition,[11] the stereochemical outcome of all cycloadducts **2A**-**5A** prepared in this investigation is assumed to have *endo*-configuration as well and was therefore not determined.[12]

As reported, cycloadduct **2A** could be aromatized with NaOH in methanol[10a] or over silica gel[10b] to give the corresponding hydroquinone **2B**. In our hands, however, application of the latter method to enolize cycloadducts **3A**-**5A** was either sluggish or totally ineffective.[13] Thus, an effort was taken to find an appropriate base for enolization, which could be both effective in the reactions performed at room temperature and also not destructive to the resulting products. The effort led us to perform the enolization reactions in dichloromethane at room temperature by using triethylamine as a promoter. In the reactions of cycloadducts **2A** and **5A**, the corresponding annulated hydroquinones **2B** and **5B** thus formed were stable and isolatable. Their identity was indicated by the disappearance of enone groups and the presence of phenolic hydroxyl groups via infrared, ^{1}H and ^{13}C NMR spectral analyses. Without purification, hydroquinones **2B** and **5B** were subsequently subjected to oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), thereby resulting in the formation of fragmented products **2D** and **5D**, respectively. However, in cases of the enolization of cycloadducts **3A** and **4A**, the reactions produced directly the corresponding polyacenoquinone esters **3D** and **4D**. Apparently, the hydroqui-

Table 1. Diels-Alder Cycloadditions of 1,4-Quinones **2-5** with 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene (**1**)



Entry	Dienophile	Cycloadduct	Yield[a]
1	**2**	 **2A**	77%
2	**3**	 **3A**	82%
3	**4**	 **4A**	92%
4	**5**	 **5A**	73%

[a] Isolated yields after recrystallization from chloroform.

nones **3B** and **4B** thereby formed in the reactions were rapidly oxidized by air to the unstable annulated 1,4-quinones, which subsequently underwent Grob-type fragmentation to afford **3D** and **4D**. Attempts of isolating hydroquinones **3B** and **4B** (or **3C** and **4C**) from the reactions performed under N_2 atmosphere were not successful. Table 2 summarizes the results of the triethylamine-promoted fragmentation of cycloadducts **2A**-**5A** to form polyacenoquinones **2D** and **5D**.

The structure of known anthraquinone ester **3D** was suggested by similar mp and the infrared (IR) spectral absorptions as those reported[9] and further supported by additional spectral analysis (^{1}H and ^{13}C NMR, and MS). The structures of polyacenoquinone esters **2D**, **4D**, and **5D** were established by spectral analysis (IR, ^{1}H and ^{13}C NMR, and MS) and supported by elemental analysis. All the fragmentation products **2D**-**5D** show one singlet at $\delta \sim 4.10$ in the ^{1}H NMR spectra and two signals at $\delta \sim 165.0$ and 53.0 in the ^{13}C NMR spectra, which together are assignable to the methoxycarbonyl group.

The unsymmetrical naphthoquinone ester **2D** has permitted us to extend the investigation of the current approach for synthesizing bis-methoxycarbonyl substituted anthraquinone and the regioselectivity in the triethylamine-promoted fragmentation reaction of the corresponding unsymmetrical cycloadduct **6A** (Scheme II). To this end, a solution of cyclic diene **1** and **2D** in toluene was heated under reflux for 4 days and the corresponding Diels-Alder cycloadduct **6A** was obtained in 86% yield after recrystallization from chloroform. The ^{1}H NMR spectrum displays three singlets for the

Scheme II

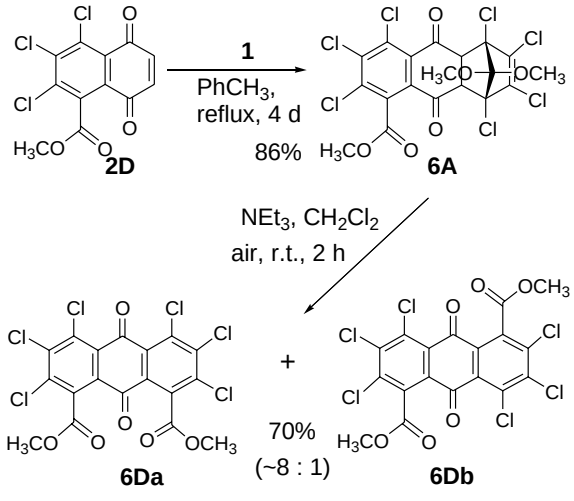
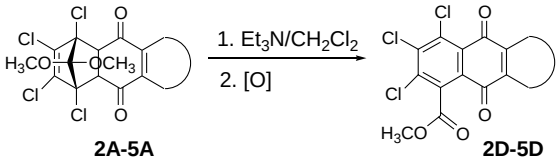
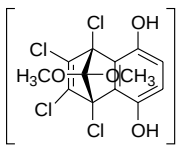
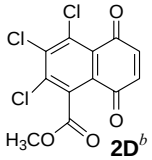
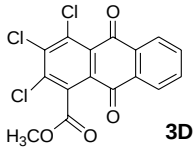
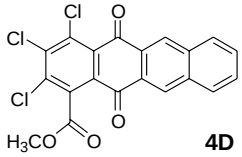
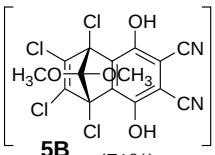
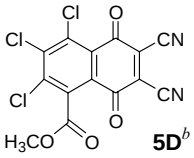


Table 2. Base-Promoted Fragmentation of Diels-Alder Cycloadducts **2A-5A** to Benzoannulated Quinones **2D-5D**



2A-5A **2D-5D**

Entry	Cycloadduct	Fragmentation Product	Yield[a]
1	**2A**	 **2B** (80%)  **2D**[b]	56%
2	**3A**	 **3D**	78%
3	**4A**	 **4D**	81%
4	**5A**	 **5B** (71%)  **5D**[b]	61%

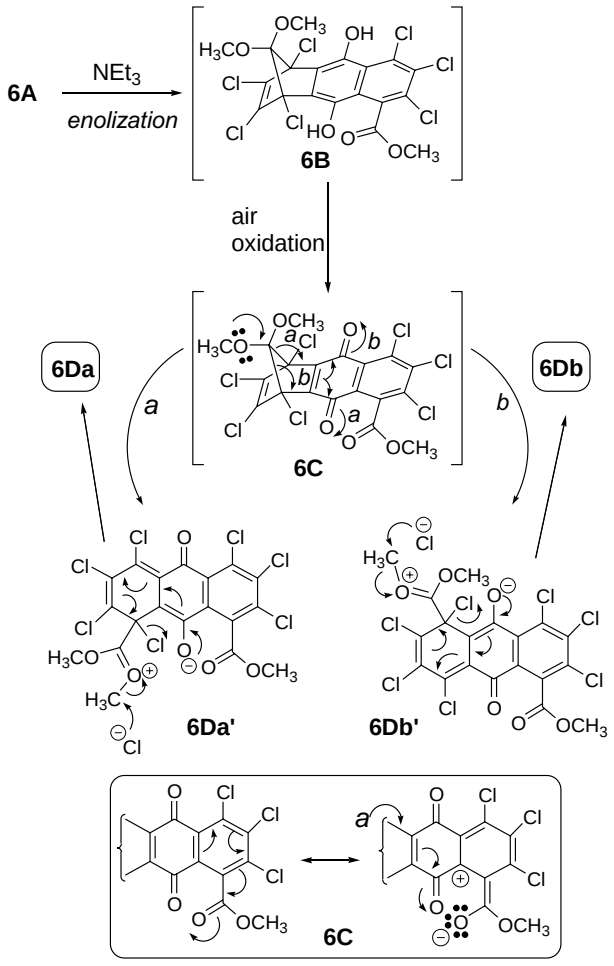
[a] Total isolated yields after recrystallization from chloroform. Yields were not optimized.
[b] Obtained by oxidation of the corresponding hydroquinone (**2B**/**5B**) with DDQ.

three chemically nonequivalent methoxyl groups, and the ^{13}C NMR spectrum has 19 lines indicating the expected dissymmetric property of **6A**. When a solution of cycloadduct **6A** in dichloromethane was treated with triethylamine for 2 h, the reaction produced two fragmented products **6Da** and **6Db** in about 8:1 ratio as indicated by the intensity of two (and only two) singlets in the ^1H NMR spectrum of crude product mixture. The major product **6Da**, which could be easily separated and purified by recrystallization from chloroform, had an elemental analysis in accordance with the molecular formula $C_{18}H_6Cl_6O_6$. The minor product **6Db**, which could only be obtained in the spectrum-pure form by repetitive recrystallization, was found to be isomeric to **6Da** by the similarity of spectral data. It is impossible to differentiate between these two isomers by ^1H NMR, IR, and MS spectral analyses, all of which are in harmony with the structures of **6Da** and **6Db**. However, one of the molecular structures of these two diester products (**6Da**) has a mirror-plane of symmetry (σ), perpendicular to the ring framework through the two carbonyl groups of the central benzoquione moiety, and the other structure (**6Db**) a center of symmetry (*i*). The major isomeric product, which shows a ten-line ^{13}C NMR spectrum containing two carbon absorptions at δ 178.6 and 178.3 attributed to these two carbonyl groups, could only be in agree-

ment with the structure of **6Da**. On the other hand, the ^{13}C NMR spectrum of the minor product **6Db** displays only nine lines with only one such absorption signal at δ 178.2; the two carbonyl groups in **6Db** are rendered chemically equivalent by inversion through a center of symmetry.

The triethylamine-promoted reaction of cycloadduct **6A** resulting in the formation of **6Da** as a major fragmentation product merits additional comment. A plausible mechanism for the formation of **6Da** and **6Db** is depicted in Scheme III. We suggest that once the annulated hydroquinone **6B** is formed from **6A** by the triethylamine-promoted enolization (aromatization), it is oxidized by air to the corresponding quinone **6C**, which is too unstable to be isolated under the reaction condition and rapidly undergoes Grob-type fragmentation (eq. 2) to form intermediates **6Da'** and **6Db'**. The fragmentation is assisted by the α,β-unsaturated carbonyl moiety and relayed by the enone C-C double bond. Presumably, the relative population of **6Da'** and **6Db'** is determined by the polarity of two carbonyl groups, which in turn depends on their relative position (*ortho*- vs *meta*-) to the existing methoxycarbonyl substituent on the trichlorinated benzene ring (insert, Scheme III). Carbonyl group *ortho* to the existing methoxycarbonyl substituent would be expected to be more electrophilic by polarization, and thus directs the direction of ring cleavage to afford **6Da** as the major product.

Scheme III



In summary, we have developed a simple, two-step preparation of chlorinated polyacenoquinone esters by the benzoannulation of various quinones using cyclic diene **1** as benzoannulating agent. The approach is based on a combination of the Diels-Alder cycloaddition and the triethylamine-promoted fragmentation of the resulting cycloadducts. The latter process consists of three reactions (enolization, oxidation, and fragmentation) that occur concurrently in one-pot. In the fragmentation reaction of the unsymmetrical cycloadduct **6A**, significant regioselectivity in forming two products **6Da** and **6Db** was observed. Further work to elucidate the effect of substituent on regioselectivity and to extend this approach toward the preparation of polyacenoquinones is underway.

EXPERIMENTAL SECTION

General

Melting points were determined in capillaries on a Thomas-Hoover apparatus and are uncorrected. Infrared (IR) spectra were recorded on a JASCO 400-plus spectrophotometer as a solid suspended in a KBr disk. ^1H and ^{13}C NMR spectra were collected on a Varian Gemini-200 or Brüker DPX-400 spectrometer using $CDCl_3$ as solvent (unless otherwise specified). All chemical shifts were expressed in δ (ppm) with reference to $CHCl_3$ (δ 7.26 for ^1H and δ 77.0 for ^{13}C). Coupling constants are reported in hertz. The number of attached hydrogen on the carbon atom was determined by the DEPT analysis. Mass (MS) spectra were obtained on a VG Trio-2000 GC/MS instrument by the EI mode unless otherwise indicated. Microanalyses were performed by the Analytical Center of Chung Hsing University, Taichung, Taiwan.

p-Benzoquinone (**2**) and 1,4-naphthoquinone (**3**) were commercially available and were purified by recrystallization. 1,4-Anthraquinone (**4**) was prepared from 1,4-hydroxyl-9,10-anthraquinone (quinizarin).[14] 2,3-Dicyano-1,4-benzoquinone (**5**) was made from commercially available 2,3-

dicyano-1,4-hydroquinone by oxidation with $Pb(OAc)_4$ in ethyl acetate.[15]

General procedure for the preparation of Diels-Alder cycloadducts 2A-6A

A solution of tetrachlorodimethoxycyclopentadiene **1** (1.1 mmol) and a quinone dienophile (**2-5**/**2D**, 1.0 mmol) in toluene (20-30 mL), under N_2 atmosphere, was heated to reflux with stirring. The progress of the reaction was monitored via thin layer chromatographic (tlc) analysis. After the reaction was completed, solvent was removed under reduced pressure and the resulting solid residue was suspended in hexane (~20 mL) with vigorous stirring for 10 min., and then filtered to remove unchanged **1**. The solid thus collected was recrystallized from chloroform to afford pure **2A-6A**. Adducts **2A** and **3A** were characterized via analysis and comparison of their ^{1}H NMR spectra and mp's with those previously reported.[11]

1,2,3,4-Tetrachloro-1,4,4a,12a-tetrahydro-1,4-dimethoxymethanonaphthacene-5,12-dione (4A)

(Yellow microcrystalline solid, 92%): mp 271-272 °C; IR (KBr) 1678 (vs), 1602 (m), 1263 (s), 1189 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 8.05 (dd, *J* = 3.3, 6.2 Hz, 2H), 7.70 (dd, *J* = 3.3, 6.4 Hz, 2H), 3.93 (s, 2H), 3.72 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0 (s), 135.2 (s), 131.4 (s), 130.1 (d), 129.8 (d), 129.5 (s), 129.1 (d), 111.5 (s), 78.1 (s), 56.0 (d), 53.1 (q), 52.2 (q); MS (EI, 70 eV) *m/z* (relative intensity) 474 (w), 472 (w), 470 (M^+, w), 439 (30), 437 (100), 435 (M^+-Cl, 81), 257 (10), 255 (14), 252 (13), 126 (31), 125 (47), 59 (21). Anal. Calcd for $C_{21}H_{14}Cl_4O_4$: C, 53.42; H, 2.99; O, 13.55. Found: C, 53.09; H, 2.87; O, 13.14.

2,3-Dicyano-5,6,7,8-tetrachloro-4a,5,8,8a-tetrahydro-5,8-dimethoxymethano-1,4-naphthoquinone (5A)

(Bright yellow microcrystalline solid, 73%): mp 164-165 °C; IR (KBr) 2228 (m), 1704 (s), 1596 (m), 1253 (s), 1193 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 2H), 3.67 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8 (s), 132.0 (s), 129.7 (s), 110.8 (s), 109.3 (s), 77.8 (s), 55.6 (d), 53.4 (q), 52.5 (q); MS (EI, 70 eV) *m/z* (relative intensity) 391 (4), 389 (39), 387 (99), 385 (M^+ - Cl, 100), 357 (12), 355 (30), 353 (29), 343 (16), 341 (15), 340 (62), 338 (59), 256 (8), 254 (9), 59 (25); Anal. Calcd for $C_{15}H_8Cl_4N_2O_4$: C, 42.69; H, 1.91; O, 15.16. Found: C, 42.43; H, 1.97; O, 15.09.

2,3,4,5,6,7,8-Heptachloro-9,10-dioxo-5,8,8a,9,10,10a-hexahydro-5,8-dimethoxymethanoanthracene-1-carboxylic acid methyl ester (6A)

(White microcrystalline solid, 86%): mp 200-201 °C; IR (KBr) 1742 (s), 1702 (s), 1600 (m), 1289 (s), 1234 (s), 1189 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 3.90 (d, *J* = 9.1 Hz, 1H), 3.87 (d, *J* = 9.1 Hz, 1H), 3.67 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0 (s), 187.9 (s), 164.4 (s), 141.1 (s), 136.9 (s), 134.8 (s), 133.7 (s), 133.0 (s), 132.9 (s), 129.6 (s, 2C), 112.1 (s), 77.6 (s), 57.5 (d), 57.1 (d), 53.4 (q), 53.2 (q), 52.3 (q); MS (EI, 70 eV) *m/z* (relative intensity) 588 (w), 584 (w), 580 (M^+, w), 555 (3), 553 (11), 551 (34), 549 (68), 547 (94), 545 (46, M^+-Cl), 289 (27), 287 (28), 259 (20), 257 (33), 255 (65), 253 (68), 209 (38), 207 (58), 206 (100), 180 (30), 178 (35), 59 (97); Anal. Calcd for $C_{19}H_{11}Cl_7O_6$: C, 39.11; H, 1.90; O, 16.45. Found: C, 38.89; H, 1.92; O, 16.06.

General procedure for the triethylamine-promoted reactions of cycloadducts 2A-6A. Preparation of polyacenoquinone esters 2D-6D

Into a stirring solution of cycloadduct (**2A-6A**, 0.5 mmol) in dichloromethane (50 mL) was dropwise added triethylamine (1 mmol) at room temperature with reaction bottle open to the air. The progress of the reaction was monitored via thin layer chromatographic (tlc) analysis. After the cycloadduct completely disappeared, the reaction mixture was cooled with an ice-water bath and quenched by the addition of saturated aqueous ammonium chloride solution. The organic layer was separated and washed sequentially with water (3 × 30 mL) and brine (30 mL). The organic layer was dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated in vacuo. The colored solid residue thus obtained was purified via recrystallization.

2,3,4-Trichloro-5,8-dioxo-5,8-dihydronaphthalene-1-carboxylic acid methyl ester (2D)

Application of the general procedure described above for the reaction of **2A** with triethylamine (reaction time: 3 h) furnished **5,6,7,8-Tetrachloro-5,8- dihydro-5,8-dimethoxymethanonaphthalene-1,4-diol (2B**) (80%) as a white powder: mp 197-198 °C (lit.[10b] 198-199 °C); IR (KBr) 3351 (m), 2946 (w), 2845 (w), 1651 (w), 1488 (s), 1455 (w), 1360 (m), 1258 (s), 1176 (m), 1155 (s), 999 (w), 807 (w), 776 cm^{-1} (s); ^{1}H NMR (400 MHz, CD_3COCD_3) δ 7.81 (s, 2H), 6.62 (s, 2H), 3.63 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 146.0 (s), 136.5 (s), 125.7 (s), 122.2 (s), 118.4

(s), 77.6 (s), 52.3 (q), 52.1 (q). This material, as obtained, was subjected to oxidation with DDQ.

Compound **2B** (0.7 g) was dissolved in dichromethane (10 mL) containing DDQ (0.4 g, 1.8 mmol). The reaction mixture was stirred until **2B** totally disappeared, and the resulting white precipitate was removed by filtration. The filtrate was concentrated to leave a yellow solid residue which was recrystallized from chloroform to afford **2D** (0.4 g, 70%) as a bright yellow crystal: mp 189-190 °C (lit.[10] 189-191 °C); IR (KBr) 1735 (s), 1680 (s), 1670 (s), 1620 (m), 1300 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 10.4 Hz, 1H), 6.94 (d, J = 10.4 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.7 (s), 181.4 (s), 165.4 (s), 141.2 (s), 140.2 (d), 137.0 (s), 136.4 (d), 135.5 (s), 133.5 (s), 129.1 (s), 127.6 (s), 53.4 (q); MS (EI, 12 eV) *m/z* (relative intensity) 322 (10), 320 (26), 318 (M^+, 28), 291 (30), 289 (96), 287 (100), 261 (4), 259 (4). Anal. Calcd for $C_{12}H_5Cl_3O_4$: C, 45.11; H, 1.58; Cl, 33.29. Found: C, 45.12; H, 1.60; Cl, 33.60.

2,3,4-Trichloro-9,10-dioxo-9,10-dihydroanthracene-1-carboxylic acid methyl ester (3D)

Application of the general procedure described above for the reaction of **3A** with triethylamine (reaction time: 38 h) afforded **3D** (bright yellow microcrystalline solid, 78%): mp 192.5-1193.5 °C (lit.[9] 196 °C); IR (KBr) 1737 (s), 1678 (s), 1615 (w), 1291 (s), 1243 (s), 1145 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.19-8.27 (m, 2H), 7.81-7.86 (m, 2H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2 (s, 2C), 165.9 (s), 141.3 (s), 136.9 (s), 135.9 (s), 135.2 (d), 134.4 (d), 133.92 (s), 133.88 (s), 131.5 (s), 130.8 (s), 129.6 (s), 127.7 (d), 127.2 (d), 53.4 (q); MS (EI, 70 eV) *m/z* (relative intensity) 372 (4), 370 (16), 368 (M^+, 15), 341 (27), 339 (100), 337 (99), 255 (17), 253 (17), 220 (31), 218 (45).

2,3,4-Trichloro-5,12-dioxo-5,12-dihydronaphthacene-1-carboxylic acid methyl ester (4D)

Application of the general procedure described above for the reaction of **4A** with triethylamine (reaction time: 18 h) afforded **4D** (81%) as a bright yellow microcrystalline solid: mp > 275 °C; IR (KBr) 1739 (s), 1686 (m), 1615 (w), 1293 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.75 (s, 1H), 8.06-8.11 (m, 2H), 7.71-7.74 (m, 2H), 4.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.22 (s), 180.16 (s), 166.1 (s), 141.3 (s), 137.0 (s), 136.1 (s), 135.6 (s, 2C), 135.0 (s, 2C), 134.1 (s), 131.9 (s), 130.8 (s), 130.3 (d), 130.2 (d), 130.1 (d), 130.0 (d), 129.8 (s), 127.7 (s), 53.4 (q); MS (EI, 70 eV) *m/z* (relative intensity) 422 (12), 420 (40), 418 (M^+, 37), 393 (6), 391 (39), 389 (100), 387 (88), 194 (35). Anal. Calcd for $C_{20}H_9Cl_3O_4$: C, 57.24; H, 2.16; O, 15.25. Found: C, 57.40; H, 2.53; O, 15.36.

2,3,4-Trichloro-6,7-dicyano-5,8-dioxo-5,8-dihydronaphthalene-1-carboxylic acid methyl ester (5D)

Application of the general procedure described above for the reaction of **5A** with triethylamine (reaction time: 3.5 h) furnished **2,3-Dicyano- 5,6,7,8-tetrachloro-5,8-dihydronaphthalene-1,4-diol (5B)** (71%) as a white powder: mp 178-179 °C (decomp.); IR (KBr) 3506 (m), 2952 (w), 2848 (w), 2232 (m), 1603 (m), 1475 (s), 1418 (m), 1215 (s), 1185 (s), 1164 (s), 1139 (s), 1011 (m), 973 (m), 756 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (s), 3.65 (s), 3.52 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1 (s), 135.8 (s), 131.1 (s), 124.3 (s), 112.0 (s), 106.0 (s), 78.2 (s), 53.7 (q), 53.4 (q).

This material **5B**, as obtained, was subjected to oxidation with DDQ by the same procedure as that used to oxidize **2B** to **2D** described above, thereby producing **5D** (86%) as a bright yellow microcrystalline solid: mp 219-220 °C; IR (KBr) 2203 (m), 1734 (s), 1629 (m), 1290 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (s), 173.1 (s), 163.8 (s), 144.1 (s), 139.6 (s), 137.4 (s), 134.5 (s), 130.3 (s), 127.9 (s), 127.0 (s), 126.2 (s), 109.7 (s), 109.2 (s), 54.0 (q); MS (EI, 70 eV) *m/z* (relative intensity) 372 (3), 370 (13), 368 (M^+, 13), 343 (3), 341 (26), 339 (83), 337 (100), 254 (25), 253 (22), 144 (23), 142 (32). Anal. Calcd for $C_{14}H_3Cl_3N_2O_4$: C, 45.50; H, 0.82; O, 17.32. Found: C, 45.36; H, 0.98; O, 17.26.

2,3,4,5,6,7-Hexachloro-9,10-dioxo-9,10-dihydroanthracene-1,8-dicarboxylic acid dimethyl ester (6Da) and 2,3,4,6,7,8-hexachloro-9,10-dioxo-9,10-dihydroanthracene-1,5-dicarboxylic acid dimethyl ester (6db)

Application of the general procedure described above for the reaction of **6A** with triethylamine (reaction time: 2 h) afforded a mixture of isomeric products **6Da** and **6Db** in ratios of 7-10:1 (total yield 70%) as a deep red solid. The major product **6Da** could be isolated in pure form via recrystallization from chloroform as a yellow microcrystalline solid: mp 249-250 °C; IR (KBr) 1740 (s), 1689 (s), 1272 (s), 1241 (s), 1142 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6 (s), 178.3 (s), 164.6 (s), 141.8 (s), 137.1 (s), 135.0 (s), 133.2 (s), 131.6 (s), 129.2 (s), 54.6 (q); MS (EI, 70 eV) *m/z* (relative intensity) 534 (4), 532 (11), 530 (13), 528 (M^+, 6), 503 (33), 502 (11), 501 (87), 499 (100), 497 (M^+ - OCH_3, 51), 468 (22), 440 (12), 236 (40), 233 (64), 179 (15), 178 (19), 177 (22). Anal. Calcd for $C_{18}H_6Cl_6O_6$: C, 40.72; H, 1.14; O, 18.08. Found: C, 40.38; H, 1.53; O,

18.22.

The red-colored mother liquid was concentrated and the resulting solid residue was recrystallized from ethyl acetate to afford **6Db** as a yellow microcrystalline solid: mp 254-255 °C; IR (KBr) 2951 (w), 2920 (w), 1736 (s), 1684 (m), 1542 (w), 1436 (m), 1388 (w), 1287 (s), 1263 (s), 1221 (s), 1143 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$) δ 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2 (s), 165.0 (s), 141.3 (s), 138.0 (s), 135.5 (s), 133.6 (s), 131.8 (s), 128.6 (s), 53.6 (q); MS (EI, 70 eV) *m/z* (relative intensity) 534 (7), 532 (16), 530 (31), 528 (M^+, 16), 503 (36), 502 (37), 501 (79), 500 (72), 499 (100), 498 (74), 497 (M^+ - OCH_3, 55), 496 (36), 468 (6), 440 (8), 233 (10), 178 (15).

ACKNOWLEDGMENT

This work was supported by the National Science Council of Taiwan. J. Y. C. thanks NSC for support through the Undergraduate Summer Research Project (NSC 85-2815-C194-01-014M).

Received May 12, 2003.

REFERENCES

1. (a) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* **1949**, *71*, 946. (b) McBee, E. T.; Crain, D. L.; Crain, R. D.; Belohlav, L. R.; Braendlin, H. P. *J. Am. Chem. Soc.* **1962**, *84*, 3557.
2. (a) Ungnade, H. E.; McBee, E. T. *Chem. Rev.* **1958**, *58*, 249. (b) McBee, E. T.; Diveley, W. R.; Burch, J. E. *J. Am. Chem. Soc.* **1955**, *77*, 385. (c) Yates, P.; Eaton, P. E. *Tetrahedron* **1961**, *12*, 13. (d) Mackenzie, K. *Tetrahedron Lett.* **1974**, 1023. (e) Jung, M. E.; Kaas, S. M. *Tetrahedron Lett.* **1989**, *30*, 641. (f) For a recent review: Khan, F. A.; Prabhudas, B.; Dash, J. *J. Prakt. Chem.* **2000**, *342*, 512.
3. For examples: (a) Eaton, P. E.; Or, Y. S.; Branca, S. J. *Tetrahedron* **1986**, *42*, 1621. (b) Fessner, W. D.; Sedelmeimer, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626. (c) Chou, T.-C.; Chuang, K.-S.; Lin, C.-T. *J. Org. Chem.* **1988**, *53*, 5168. (d) Mehta, G.; Padma, S. *J. Org. Chem.* **1991**, *56*, 1298. (e) Forman, M. A.; Dailey, W. P. *J. Org. Chem.* **1993**, *58*, 1501. (f) Chou, T.-C.; Yeh, Y.-L.; Lin, G.-H. *Tetrahedron Lett.* **1996**, *37*, 8779. (g) Chou, T.-C.; Lin, G.-H.; Yeh, Y.-L.; Lin, K.-C. *J. Chin. Chem. Soc.* **1997**, *44*, 477. (h) Khan, F. A.; Dash, J. *J. Am. Chem. Soc.* **2002**, *124*, 2424. (i) Khan, F. A.; Dash, J.; Sahu, N.; Sudheer, Ch. *J. Org. Chem.* **2002**, *67*, 3783.
4. For examples: (a) Mehta, G.; Mohal, N. *Tetrahedron Lett.* **1998**, *39*, 3281. (b) Mehta, G.; Reddy, D. S. *Tetrahedron Lett.* **1999**, *40*, 9137. (c) Mehta, G.; Reddy, D. S.; Ramesh, S. S.; Tatu, U. *Tetrahedron Lett.* **1999**, *40*, 9141. (d) Mehta, G.; Reddy, D. S. *J. Chem. Soc. Perkin Trans. 1* **2000**, 1399.
5. (a) Grob, C. A.; Baumann, W. *Helv. Chim. Acta* **1955**, *38*, 594. (b) Wharton, P. S.; Hiegel, G. A. *J. Org. Chem.* **1965**, *30*, 3254. (c) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1. (d) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535. (e) Caine, D. *Org. Prep. Proced. Int.* **1988**, *20*, 1.
6. (a) Hoch, P. E. *J. Org. Chem.* **1961**, *26*, 2066. (b) Kagi, R. I.; Johnson, B. L. *Aust. J. Chem.* **1975**, *28*, 2189.
7. Mitchell, R. H.; Chaudhary, M.; Kamada, T.; Slowey, P. D.; Williams, R. V. *Tetrahedron* **1986**, *42*, 1741.
8. (a) Dickmann, J. *J. Org. Chem.* **1963**, *28*, 2880. (b) Mackenzie, K. *J. Chem.* Soc. **1964**, 5710. (c) Lustgarten, R. K.; Richey, H. G. *J. Am. Chem. Soc.* **1974**, *96*, 6393. (d) Sunko, D. E.; Lovrić, Z.; Vančik, H. *J. Chem. Soc. Chem. Commun*. **1985**, 1598.
9. (a) Kniel, P. *Helv. Chim. Acta* **1963**, *52*, 492. (b) Kniel, P. *Helv. Chim. Acta* **1965**, *91*, 837. See also: O′Connor, U.; Rosen, W. *J. Org. Chem.* **1980**, *45*, 1824.
10. (a) Mehta, G.; Padma, S.; Venkatesan, K.; Begum, N. S.; Moorthy, J. N. *Indian J. Chem.* **1992**, *31B*, 473. (b) Marchand, A. P.; Alihodzic, S.; Shukla, R. *Synth. Commun*. **1998**, *28*, 541.
11. (a) Marchand, A. P.; Chou, T.-C. *J. Chem. Soc. Perkin Trans. 1*, **1973**, 1948. (b) Chou, T.-C.; Chiou, J.-H. *J. Chin. Chem. Soc.* **1986**, *33*, 27. (c) Chou, T.-C.; Hong, P.-C.; Wu, Y.-F.; Chang, W.-Y.; Lin, C.-T.; Lin, K.-J. *Tetrahedron* **1996**, *52*, 6325.
12. We also noticed the high sensitivity of cycloadduct **5A** toward laboratory illumination and took precaution by wrapping the reaction flask with aluminum foil to minimize contact with light during preparation.
13. Comparable results were found for the reactions in which silica gel was replaced by aluminum oxide.
14. (a) Bedworth, P. V.; Perry, J. W.; Marder, S. R. *J. Chem. Soc. Chem. Commun.* **1997**, 1353. (b) Patney, H. K. *Synthesis* **1986**, 326.
15. (a) Adams, R.; Whitehill, L. N. *J. Am. Chem. Soc.* **1941**, *63*, 2073. (b) Perrier, S.; Kochi, J. K. *J. Chem. Soc.Perkin Trans 2* **1993**, 825.