with chloroform (2 mL). Organic phases were combined and evaporated, and the residue was subjected to crystallization or purification on a silica gel column. Alternatively, the protected phospholipids can be purified on silica gel columns and then subjected to a deprotection step.

General Procedure for Synthesis of Phospholipid Analogues 5 and 6. To a crude reaction mixture containing the H-phosphonate 3 was added sulfur (2 equiv) in pyridine/toluene (1:1, v/v, 1 mL) or selenium (2 equiv) in dioxan (1 mL), and the suspension was stirred for 2 and 10 h, respectively. The reaction mixtures were diluted with chloroform (30 mL) and washed with water or with 0.1 TEAB. Further workup and deprotection were the same as described for 4 with the exception that the deprotection was carried out in the presence of 1,2-ethanedithiol (10 equiv).

1,2-Dipalmitoyl-*sn*-glycero-3-H-phosphono-*N*-(*tert*-butoxycarbonyl)ethanolamine (3b). Column chromatography: silica gel; eluent, toluene/ethyl acetate (1:1, v/v). Yield 98%. $[\alpha]^{20}_{D}$ +2.3° (*c* 2.6, CH_2CL_2). R_f 0.60 (system F). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-phosphocholine (4a). Column chromatography: silica gel; eluent, $CHCl_3/MeOH/H_2O$ (66:33:4, v/v). Yield 80%. $[\alpha]^{20}_{D}$ +7.7° (*c* 2.0, $CHCl_3/MeOH$, 1:1). R_f 0.45 (system B). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-phosphoethanolamine (4b). Column chromatography: silica gel; eluent, $CHCl_3/MeOH/H_2O$ (100:15:1, v/v) and then $CHCl_3/MeOH/H_2O$ (95:35:2, v/v). Yield 86%. $[\alpha]^{20}_{D}$ +12.3° (*c* 2.2, $CHCl_3/MeOH$, 9:1). R_f 0.50 (system A). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-phospho-L-serine (4c). Column chromatography: silica gel; eluent, $CHCl_3/MeOH/H_2O$ (65:25:4, v/v). Yield 81%. $[\alpha]^{20}_{D}$ +12.5° (*c* 1.5, $CHCl_3/MeOH/H_2O$, 65:25:4, v/v). R_f 0.40 (system B). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-thiophosphoethanolamine (5b). Column chromatography: silica gel; eluent, $CHCl_3/MeOH$ (5:1, v/v). Yield 93%. $[\alpha]^{20}_{D}$ +17.5° (*c* 1.3, $CHCl_3/MeOH$, 1:1, v/v). R_f 0.49 (system D). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-thiophosphocholine (5c). Column chromatography: silica gel; eluent $CHCl_3/MeOH$ (1:1, v/v). Yield 86%. $[\alpha]^{20}_{D}$ +16.0° (*c* 2.0, $CHCl_3$). R_f 0.60 (system C). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-selenophospho-*N*-(*tert*-butylcarbonyl)ethanolamine (6a). Column chromatography: silica gel; eluent, $CHCl_3/MeOH$ (6:1, v/v). Yield 98%. R_f 0.55 (system E). For the ^{13}C and ^{31}P NMR data, see Table I.

1,2-Dipalmitoyl-*sn*-glycero-3-selenophosphoethanolamine (6b). Column chromatography: silica gel; eluent, $CHCl_3/MeOH$ (6:1, v/v). Yield 56%. $[\alpha]^{20}_{D}$ +17.6° (*c* 1.6, $CHCl_3/MeOH$, 2:1, v/v). R_f 0.37 (system E). For the ^{13}C and ^{31}P NMR data, see Table I. Anal. Calcd $C_{37}H_{74}O_7PNSe$: C, 58.8; H, 9.9; N, 1.9. Found: C, 58.5; H, 9.9; N, 1.7.

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Steady-State and Laser Flash Photolysis Studies of Norbornenobenzoquinones and Their Diels–Alder Adducts[1]

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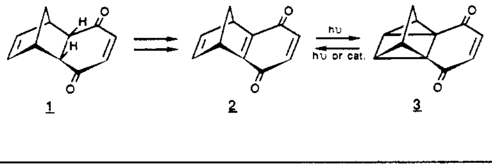
Results of a photochemical study based on nanosecond laser flash photolysis and steady-state photolysis are reported for several norbornenobenzoquinones and their rigid Diels–Alder adducts. Products isolated from steady-state photolysis of a few representative cases suggest that the preferred mode is intramolecular [2 + 2] cycloaddition wherever feasible, and triplets have been implicated in this photoreaction. The 337.1-nm laser pulse excitation of the substrates in benzene gave rise to triplets (λ_{max}^{T} = 390–580 nm), characterized by short lifetimes (21 ns–1.05 μs) in fluid solutions at room temperature. The triplets were efficiently quenched by oxygen, ferrocene, *p*-methoxyphenol, HTEMPO, and azulene, but they exhibited reluctant quenching behavior toward DMHD and triethylamine. The lower limits of triplet yields ($\phi_{T,lim}$) for most of the substrates were measured by energy transfer to 9,10-diphenylanthracene (DPA). In some cases, the efficiency of energy transfer to DPA in benzene appeared to be small, probably owing to reversible charge transfer interaction competing favorably with energy transfer.

Introduction

The interesting tricyclic quinone 2 (2,3-norbornenobenzoquinone),[3a,b] readily available from the endo adduct 1 of 1,3-cyclopentadiene and *p*-benzoquinone, has not received much attention except for a few studies by Cookson and co-workers.[3c–e] Recently, some of us[4] have demonstrated the synthetic potential of 2 through Diels–Alder chemistry to prepare novel, strained polycyclic systems. In continuation, we became interested in utilizing the photochemistry of 2 and related quinones to gain access to highly strained quadricyclane derivatives 3. In general,



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(1) Document No. NDRL-3114 from the Notre Dame Radiation Laboratory.

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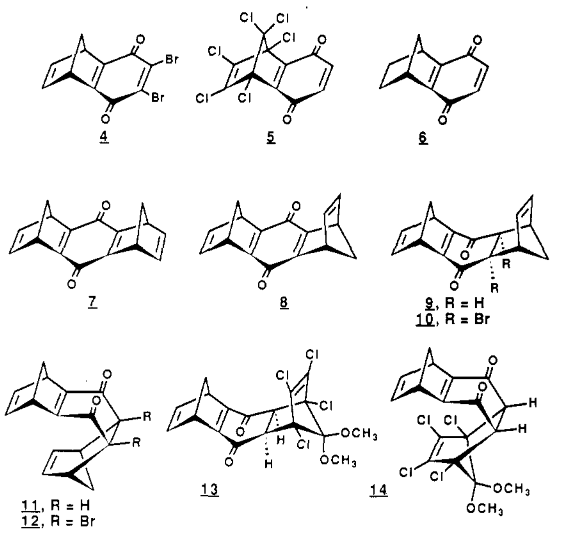
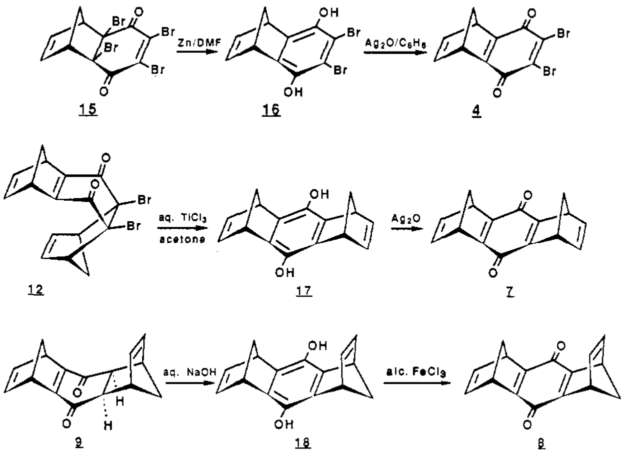
Chart I



Scheme I

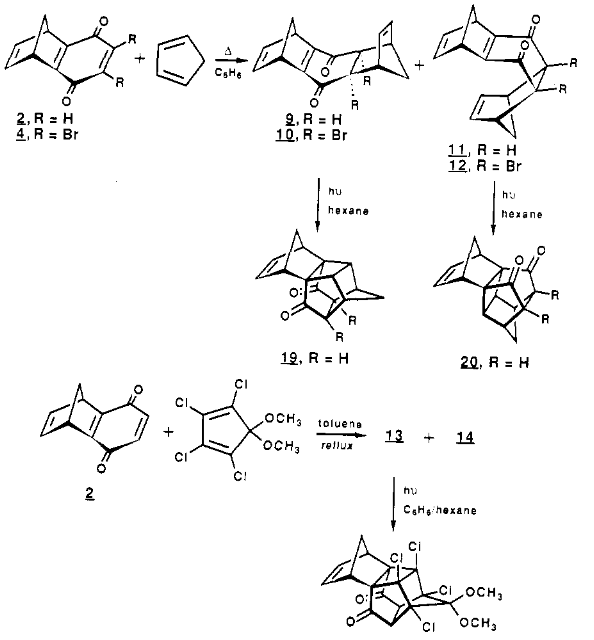


the photochemistry of norbornadiene derivatives leading to quadricyclanes has been of current interest from the viewpoint of solar energy storage.[5] As reported earlier[3c] and also observed in the present study, the irradiation of 2 under a variety of conditions gave only intractable, polymeric materials. Recently, however, a report by Suzuki et al.[6] has appeared on isomerization of certain norbornenonaphthoquinones and norbornenobenzoquinones to the corresponding quadricyclanes. Because of the photochemical significance, we became interested in a nanosecond laser flash photolysis study of 2, related quinones and their Diels–Alder adducts (Chart I). The results of this time-resolved study combined with the preparative photochemistry in representative cases are presented in this paper.

Results and Discussion

1. Preparative Chemistry. The norbornenoquinones 2, 5, and 6 were prepared as per reported procedures,[3c,d] whereas the dibromo derivative 4 was prepared as per the pathway shown in Scheme I. All these compounds were fully characterized on the basis of their ^{1}H NMR and ^{13}C NMR spectra (vide Experimental Section). Diels–Alder reaction between 1,3-cyclopentadiene and the quinones 2 and 4 gave a mixture of endo,anti and endo,syn adducts 9 and 11 (35:65)[3c] and 10 and 12 (38:62), respectively. These adducts were separated by chromatography and characterized spectroscopically. Structures 9 and 11 were further confirmed through their intramolecular [2 + 2] photocycloaddition to the corresponding heptacyclic caged compounds 19 and 20, respectively (Scheme II). Addition of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene to 2 furnished the endo,anti and endo,syn adducts 13 and 14, respectively, in the ratio of 77:23. Irradiation of the major component 13 led to the formation of the [2 + 2] photocycloadduct 21 (Scheme II).

Scheme II



The syn-bisnorbornenoquinone 7 was prepared from the endo,syn adduct 12 of the dibromoquinone 4 and cyclopentadiene, as shown in Scheme I. The orange-yellowish 7 exhibited a five-line ^{13}C NMR spectrum, with diagnostic signals at δ 48.1, 73.9, 145.7, 160.3, and 181.1. The *anti*-bisnorbornenoquinone 8 was prepared from the endo,anti adduct 9 of quinone 2 and cyclopentadiene,[3c] as shown in Scheme II. The glistening orange quinone 8 also exhibited a five-line ^{13}C NMR spectrum with signals at δ 48.1, 74.0, 142.7, 160.3, and 181.1. The two quinones 7 and 8 had nearly identical IR, ^{1}H NMR, and ^{13}C NMR spectra.

2. Laser Flash Photolysis Studies. Upon 337.1-nm laser flash photolysis, benzene solutions of substrates 2, 4–14 produce absorbance changes due to the formation of phototransients that are best characterized as triplets. Representative transient spectra and kinetic traces are shown in Figure 1. The transients decay by clean first-order kinetics over microseconds. In most cases, the decay lifetimes were measured as a function of the ground-state concentration of the substrates, and the intrinsic lifetimes were obtained by extrapolation to the zero concentration. The kinetics and spectral data are summarized in Table I.

The triplet assignment of the observed transients was based on their quenching behavior toward various reagents (see Table I), well-recognized for their efficient interaction

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Table I. Spectral and Kinetics Data of the Triplets of Norbornenobenzoquinone and Related Systems in Benzene at 298 K

				k_q^T,[b] 10^9 M^{-1} s^{-1}						
substrate	λ_{max}^T,[a] nm	τ_T,[b] μs	$\phi_{T,lim}$	O_2	HTEMPO[c]	ferrocene	azulene	PMP[c]	DMHD[c]	TEA[c]
2	510	0.79	0.7	1.8	3.4	11.0	3.9	7.9	0.45	0.46
4	530	0.054[d]	*e*	0.85	5.2	12.0	18.0	11.0	*f*	2.5
5	580	0.24[d]	*e*	1.5	5.9	14.0	12.0	10.0	7.4	9.8
6	470	1.6	1.0	1.3	8.2	14.0	11.0	11.0	4.8	8.3
7	550	0.76[d]	*e*	3.0	4.8	12.0	*f*	11.0	<0.01	0.024
8	550	0.67[d]	*e*	1.7	3.0	7.4	*f*	7.5	<0.01	0.031
9	420	0.25	0.8	2.6	0.59	3.4	1.5	2.4	<0.01	<0.01
10	420	0.021[d]	*e*	2.8	*f*	6.7	*f*	*f*	*f*	*f*
11	390	0.39	0.9	2.9	0.97	3.5	*f*	1.9	<0.01	<0.01
12	420	0.080	0.6	1.7	1.4	7.4	*f*	3.6	*f*	<0.01
13	410	0.55	0.9	1.3	1.2	5.3	2.8	1.8	<0.01	<0.01
14	400	0.54	1.0	1.9	1.2	5.3	*f*	2.6	<0.01	<0.01

[a] ±5 nm. [b] ±15%. [c] HTEMPO, 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy; PMP, *p*-methoxyphenol; DMHD, 2,5-dimethyl-2,4-hexadiene; TEA, triethylamine. [d] These lifetimes were measured at a single concentration (5 mM); the others were obtained by extrapolation to zero concentration. [e] No 9,10-diphenylanthracene triplet was observed in energy transfer experiments in these cases (see text). [f] The quenching experiments were not done in these cases.

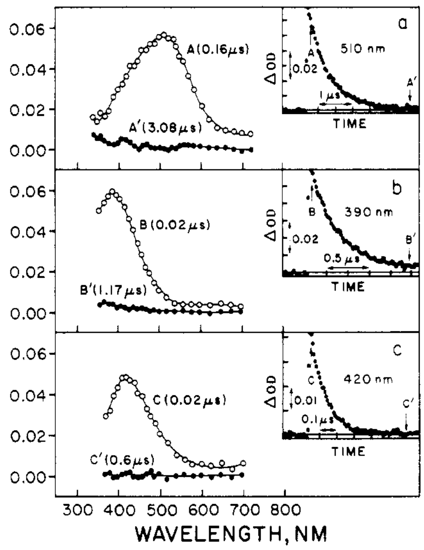

Figure 1. Transient absorption spectra at the indicated times following 337.1-nm laser pulse excitation of (A,A') **2**, (B,B') **11** and (C,C') **12** in deaerated benzene at 298 K (absorbances of solutions = 0.5–0.8 in 2-mm cell at 337.1 nm). Insets: representative kinetic traces for decay of transient absorption at the respective wavelength maximum as observed for (a) **2**, (b) **11**, and (c) **12** in benzene.

with triplets in general. In addition, we could observe the sensitized formation of 9,10-diphenylanthracene (DPA) triplet when benzene solutions of the substrates were flash photolyzed with 425-nm laser pulses in the presence of 1–8 mmol of DPA. Note that at the concentrations used, the ground state of DPA did not absorb significantly at the laser excitation wavelength (425 nm) and, moreover, that the intersystem crossing efficiency of DPA is negligible.[7] In fact, using the triplet formation of fluorenone in benzene as the actinometer ($\phi_T = 0.94$)[8] and monitoring the DPA triplet ($\lambda_{max} = 450$ nm) produced as a result of energy transfer from fluorenone and substrate triplets in optically matched solutions, we could measure the lower limits of triplet yields ($\phi_{T,lim}$) of the substrates. The limiting nature of the triplet yield data arose from the possibility that reversible electron transfer could be an efficient pathway for the quenching of triplets in question by DPA (see later). The data concerning $\phi_{T,lim}$ and bimolecular rate constants for triplet quenching are given in Table I.

The involvement of triplets in the observed photochemistry was established by studying the quenching effect of ferrocene under steady-state lamp excitation. Benzene solutions of **9** and **11** were irradiated at 366 nm for a given period of time in the presence of varying concentrations of ferrocene (0–2.5 mmol), and the loss of the starting material was monitored spectrophotometrically. The slopes of the Stern–Volmer plots for quenching agreed reasonably well (within ±40%) with $k_q^T\tau_T$ values that were calculated from triplet lifetimes observed in the solutions used (in the absence of ferrocene) and the rate constants for ferrocene quenching (Table I). This result implies that the photochemistry of **9** and **11** is mediated by their triplets. In the case of these Diels–Alder adducts, caged compounds (**19** and **20**) result from steady-state photoexcitation. Mention may be made in this connection that norbornadiene undergoes efficient conversion to quadricyclane under triplet sensitization.[9]

On the basis of the data in Table I, the following observations can be made. First, the T–T absorption maxima of the norbornenoquinones (λ_{max}^T = 510–580 nm) are considerably red-shifted relative to those of their Diels–Alder adducts (λ_{max}^T = 390–410 nm). Also, the λ_{max}^T of the parent norbornenoquinone **2** is longer than that of the related benzoquinone **6**, suggesting the importance of π-overlap among the p orbitals of the quinone moiety and the additional double bond in the former. An analogous effect is noted in the T–T spectra of **7** and **8** versus **2**. Second, the lifetimes are all short and lie in the submicrosecond domain (except **6**). A slight relative shortening in triplet lifetime is observed for the systems for which the intramolecular photochemistry has been observed (i.e., **9**, **11**, and **13**). However, a more dramatic effect is noted for the bromine-containing systems (i.e., **4**, **10**, and **12**). The enhanced triplet decay for these systems is not due to the cleavage of C–Br bonds, because in laser flash experiments no transient absorptions attributable to the Br–C_6H_6 complex (λ_{max} = 550 nm, ϵ = 23 700 M^{-1} cm^{-1})[10] are observed. Apparently, the bromine atoms introduce a heavy-atom effect that enhances the $T_1 \rightarrow S_0$ process via a spin–orbit coupling mechanism. Third, the bimolecular rate constants for triplet quenching are mostly in the limit of diffusion control. While the energy transfer mechanism

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is definitely operative with some of the quenchers (namely, oxygen, ferrocene, and azulene), the charge transfer mechanism can be viable for many of the quenchers used. The quinones are good electron acceptors ($E_{1/2}^{\mathrm{red}}$ for *p*-benzoquinone is −0.48 V vs SCE in acetonitrile)[11] and, except O_2, the quenchers in Table I are potentially good electron donors ($E_{1/2}^{\mathrm{ox}}$ are 0.3–1.2 V vs SCE in acetonitrile).[10] Thus, in order to have favorable charge transfer interactions in the worst case, the triplet energies of the substrates are required to be in the vicinity of 40 kcal mol^{-1}. On the basis of the location of the lowest lying weak absorption band systems (assigned to $\pi^* \leftarrow n$ transitions) and the low singlet-triplet separation ($\leq$10 kcal mol^{-1}) expected for (n,π^*) states,[12] we locate the E_T's of the substrates above this value. Fourth, some of the substrates, namely, **4**, **5**, and **10**, did not produce any acceptor triplet upon quenching by DPA. Also, for some of the other systems, particularly **7** and **8**, the efficiency of energy transfer to DPA appeared to be small (as judged from the intensity of donor triplet absorbance). It appears that in these cases the reversible charge transfer interaction competes favorably with or dominates over energy transfer.

Experimental Section

All melting points are uncorrected and were determined on a Büchi SMP 20 apparatus. The spectra were recorded on the following spectrometers: Perkin-Elmer Model 297 (IR), Cary 219 (UV–visible), Perkin-Elmer Lambda Array 3840 (UV-visible), JEOL FX 100 (^{1}H and ^{13}C NMR), Hitachi RMU-6E (single-focusing) (mass), and Finnigan MAT Model 8430 (mass). Steady-state irradiations for preparative photochemistry were carried out with a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketted immersion well. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold label solvents were used for laser studies. The laser pulse excitations were carried out at 337.1 nm (2–3 mJ/pulse, ~8 ns, Molectron UV-400) or 425 nm ($\leq$12 mJ/pulse, ~6 ns, Quanta-Ray DCR-1, Nd-YAG coupled with PDL-1 dye laser). Kinetic spectrophotometers and data collection systems are described elsewhere.[13]

1,4-Dihydro-1,4-methanonaphthalene-5,8-dione (2,3-Norbornenoquinone) (2).[3b] Compound **2** was prepared as per a reported procedure,[3b] mp 66 °C (lit.[3b] mp 66 °C): IR $\nu_{\max}$ (KBr) 1640, 1580, 1305, 720 cm^{-1}; UV $\lambda_{\max}$ (methanol) 255 nm (ϵ 18 160) and 386 (590); ^{1}H NMR ($CDCl_3$) δ 2.28 (2 H, m), 4.08 (2 H, m), 6.56 (2 H, s), 6.84 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 48.4 (d), 73.8 (t), 135.8 (d), 142.6 (d), 160.8 (s), 184.1 (s).

6,7-Dibromo-1,4-dihydro-1,4-methanonaphthalene-5,8-dione (4). The Diels–Alder adduct **15**[14] (10 g, 0.02 mol) of 1,3-cyclopentadiene and bromanil was dissolved in 15 mL of dry dimethylformamide (DMF) in a three-necked round-bottomed flask under nitrogen atmosphere. To this solution was added zinc dust (6.6 g, 0.1 mol) gradually, and the reaction mixture was stirred vigorously at room temperature for 5 h. The mixture was filtered through a Celite pad, and the filtrate was diluted with ether (300 mL). The organic layer was washed with water (5 × 75 mL) and brine and dried over sodium sulfate. Removal of the solvent gave the crude aromatic diol **16** (6.7 g), which was used as such for the subsequent step.

The crude diol **16** (6.7 g) was dissolved in 50 mL of dry benzene and stirred vigorously with silver(I) oxide (6.0 g, 0.256 mol) and anhydrous sodium sulfate (6.0 g) at room temperature (25 °C). The reaction mixture turned yellow immediately, and after 1 h of stirring, it was filtered. Removal of the solvent from the filtrate under vacuum gave the crude quinone, which was chromatographed on silica gel (200 g). Elution with a mixture (1:9) of ethyl acetate and hexane gave **4** (3.5 g, 55%), mp 166 °C, after recrystallization from a mixture of dichloromethane and hexane: IR $\nu_{\max}$ (KBr) 1665, 700 cm^{-1}; UV $\lambda_{\max}$ (methanol) 290 nm (ϵ 14 000), 340 (1000), 402 (230); ^{1}H NMR ($CDCl_3$) δ 2.34 (2 H, m), 4.16 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.86 (2 H, dd, $J_1 = J_2 = 2$ Hz). Anal. Calcd for $C_{11}H_6Br_2O_2$: C, 40.04; H, 1.83. Found: C, 40.0; H, 1.80.

1,4-Dihydro-1,2,3,4,9,9-hexachloro-1,4-methanonaphthalene-5,8-dione (5). Compound **5** was prepared by a reported procedure,[3c] mp 109 °C (lit.[3c] mp 119 °C): IR $\nu_{\max}$ (KBr) 3050, 1660, 1600, 1570, 1290, 1090, 830, 680 cm^{-1}; UV $\lambda_{\max}$ (methanol) 250 nm (11360), 310 (590), 370 (150); ^{1}H NMR ($CDCl_3$) δ 6.68; ^{13}C NMR ($CDCl_3$) δ 81.8, 116.2, 136.3, 138.1, 146.7, 180.2.

1,2,3,4-Tetrahydro-1,4-methanonaphthalene-5,8-dione (6). Compound **6** was prepared as per a reported procedure,[3c] mp 40 °C (lit.[3d] mp 40 °C): IR $\nu_{\max}$ (KBr) 1640, 1570, 1000, and 830 cm^{-1}; UV $\lambda_{\max}$ (methanol) 255 nm (ϵ 16 450), 358 (880); ^{1}H NMR ($CDCl_3$) δ 1.12–1.96 (6 H, m), 3.48 (2 H, br s), 6.56 (2 H, s).

Irradiation of 2.[3c] A solution of the quinone **2** in hexane was irradiated for 3 h, with use of a Pyrex filter. A white polymeric material precipitated, which did not yield any product on workup. A similar observation has been reported earlier.[3c]

Reaction of 2,3-Norbornenoquinone (2) with Cyclopentadiene.[3c] Excess of cyclopentadiene (800 mg, 12 mmol) was added to a solution of the quinone **2** (1.0 g, 5.8 mmol) in benzene, and the reaction mixture was stirred at room temperature for 30 min. Removal of the solvent under vacuum gave a residual solid, which on washing with hexane to remove the excess of cyclopentadiene gave a mixture (35:65, estimated by ^{1}H NMR spectrum) of the endo,anti adduct **9** and endo,syn adduct **11** in quantitative yield (lit.[3c] reports a 20:80 ratio of **9** and **11**, respectively, based on separation by column chromatography and fractional crystallization). The product mixture was chromatographed on a silica gel (50 g) column. Elution with a mixture (1:20) of ethyl acetate and hexane gave the endo,anti adduct, 1α,4α,5β,8β,8aα,10aα-hexahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**9**), mp 153–155 °C, after recrystallization from a mixture of dichloromethane and hexane (lit.[3c] mp 153 °C): IR $\nu_{\max}$ (KBr) 1640, 730 cm^{-1}; UV $\lambda_{\max}$ (methanol) 266 nm (ϵ 7150), 308 (1350); ^{1}H NMR ($CDCl_3$) δ 1.48 (2 H, AB q, $J_1 = J_2 = 9$ Hz), 2.1 (2 H, AB q, $J_1 = J_2 = 7$ Hz), 3.15 (2 H, dd, $J_1 = J_2 = 2$ Hz), 3.48 (2 H, br s), 3.92 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.0 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.76 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 48.4, 48.8, 49.4, 51.1, 73.7, 134.9, 142.5, 167.1, 195.6.

Further elution of the column with the same solvent mixture gave the endo,syn adduct, 1α,4α,5α,8α,8aβ,10aβ-hexahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**11**), mp 155 °C (lit.[3c] mp 152–154 °C): IR $\nu_{\max}$ (KBr) 1640, 710 cm^{-1}; UV $\lambda_{\max}$ (methanol) 263 nm (8880), 300 (2130); ^{1}H NMR ($CDCl_3$) δ 1.46 (2 H, m), 2.18 (2 H, m), 3.26 (2 H, m), 3.46 (2 H, br s), 3.98 (2 H, dd, $J_1 = J_2 = 2$ Hz), 5.79 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.78 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$), 48.2 (2 C), 48.7, 50.5, 72.3, 134.5, 142.7, 166.9, 195.6.

Irradiation of the Endo,Anti Adduct 9. *syn*-Heptacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{2,6}.0^{7,11}]hexadec-13-ene-3,10-dione (19).[3c] A solution of the enedione **9** (50 mg, 0.2 mmol) in hexane (125 mL) was irradiated for 5 h, with use of a Pyrex filter. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel column (5 g). Elution with a mixture (1:10) of ethyl acetate and hexane gave **19** (30 mg, 60%), mp 153 °C, on recrystallization from a mixture of dichloromethane and hexane (lit.[3c] mp 153 °C): IR $\nu_{\max}$ (KBr) 1730, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (2 H, AB q, $J_1 = J_2 = 9$ Hz), 1.97 (2 H, m), 2.52 (2 H, br s), 2.6–3.0 (6 H, m), 6.2 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 38.1, 39.9, 40.4, 43.0, 44.2, 53.8, 62.3, 137.7, 217.6.

Irradiation of the Endo,Syn Adduct 11. *anti*-Heptacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{2,6}.0^{7,11}]hexadec-13-ene-3,10-dione (20).[3c] Irradiation of the enedione **11** and workup as in the earlier case gave a 60% yield of **20**, mp 140–142 °C (lit.[3c] mp 125–133 °C): IR $\nu_{\max}$ (KBr) 1740, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.54 (2 H, AB q, $J_1 = J_2 = 9$ Hz), 1.94 (2 H, AB q, $J_1 = J_2 = 12$ Hz), 2.4–3.0 (8, H, m), 6.36 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 39.3,

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41.2, 41.9, 44.0, 50.9, 55.9, 62.2, 136.8, 213.8.

Reaction of the Dibromoquinone 4 with Cyclopentadiene. To a solution of 4 (800 mg, 2.42 mmol) in benzene (25 mL) was added cyclopentadiene (319 mg, 4.8 mmol), and the mixture was refluxed for 4 h. Removal of the solvent under vacuum gave a residual solid, which on washing with hexane to remove the excess of cyclopentadiene gave a 78% yield of a mixture (62:38, estimated by ^{1}H NMR spectrum) of the endo,syn adduct 12 and endo,anti adduct 10. The mixture was chromatographed on silica gel (25 g), and elution with a mixture (1:20) of ethyl acetate and hexane gave the endo,syn adduct, 10aβ,8aβ-dibromo-1α,4α,5α,8α-tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**12**), mp 171 °C, on recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1645, 1600, 740 cm^{-1}; UV λ_{max} (methanol) 258 nm (ϵ 9000), 320 (1060); ^{1}H NMR (CDCl$_3$) δ 2.28 (2 H, s), 2.32 (2 H, AB q, $J_1 = J_2 = 12$ Hz), 3.67 (2 H, dd, $J_1 = J_2 = 2$ Hz), 4.0 (2 H, br s), 5.92 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.76 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR (CDCl$_3$) δ 45.9, 49.8, 55.6, 69.5, 72.8, 137.2, 142.1, 166.6, 186.1. Anal. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05. Found: C, 48.30; H, 3.04.

Further elution of the column with the same solvent mixture gave the endo,anti adduct, 10aα,8aβ-dibromo-1α,4α,5β,8β-tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**10**), mp 199 °C, on recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1675, 1600, 800, 720 cm^{-1}; UV λ_{max} (methanol) 270 nm (ϵ 6770), 320 (990); ^{1}H NMR (CDCl$_3$) δ 2.28 (2 H, s), 2.36 (2 H, AB q, $J_1 = J_2 = 12$ Hz), 3.70 (2 H, dd, $J_1 = J_2 = 2$ Hz), 4.14 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.12 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.94 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR (CDCl$_3$) δ 46.2, 49.6, 55.7, 73.2, 76.7, 137.3, 142.7, 166.7, 185.4. Anal. Calcd for $C_{16}H_{12}O_2Br_2$: C, 48.12; H, 3.05. Found: C, 48.32; H, 3.02.

1α,4α,5α,8α-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (7). To a solution of the *endo,syn*-dibromo adduct 12 (100 mg, 0.25 mmol) in 5 mL of acetone was added 30% TiCl$_3$ (3 mL), under nitrogen atmosphere, and the reaction mixture was stirred for 30 min at room temperature. The mixture was poured into brine (20 mL), and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with sodium bicarbonate solution and brine and later dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave the crude diol 17 (60 mg; IR ν_{max} (KBr) 3300, 1560, 1300 cm^{-1}).

The diol 17 (50 mg) was dissolved in 3 mL of ethyl acetate and stirred vigorously with silver(I) oxide (50 mg) and anhydrous sodium sulfate (75 mg) for 30 min. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture of dichloromethane and hexane to give the *syn*-bisnorbornenoquinone adduct 7 (48 mg, 95%), mp 205 °C: IR ν_{max} (KBr) 1640, 1550, 1180, 750 cm^{-1}; UV λ_{max} (methanol) 278 nm (ϵ 14300), 330 (1000), 430 (150); ^{1}H NMR (CDCl$_3$) δ 2.28 (4 H, br s), 4.04 (4 H, br s), 6.8 (4 H, dd, $J_1 = J_2 = 1.5$ Hz); ^{13}C NMR (CDCl$_3$) δ 48.1, 73.9, 142.7, 160.3, 181.1. Mol wt calcd for $C_{16}H_{12}O_2$ 236.0837, found (high-resolution mass spectrometry) 236.0833.

1α,4α,5β,8β-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (8).[3c] Compound 8 was prepared from the endo,anti adduct 9 as per a reported procedure,[3c] mp 250 °C dec (lit.[3c] mp 250 °C dec): IR ν_{max} (KBr) 1640, 1550, 1180, 750 cm^{-1}; UV λ_{max} (methanol) 283 nm (ϵ 16380), 348 (600), 430 (150); ^{1}H NMR (CDCl$_3$) δ 2.24 (4 H, m), 4.0 (4 H, m), 6.84 (4 H, dd, $J_1 = J_2 = 1.5$ Hz); ^{13}C NMR (CDCl$_3$) δ 48.1, 74.0, 142.7, 160.3, 181.1.

Reaction of the Quinone 2 with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. A mixture of 2 (5.0 g, 0.03 mmol) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (8.0 g, 0.03 mmol) in dry toluene (30 mL) was refluxed for 12 h. Removal of the solvent under vacuum and washing of the residual solid with hexane gave a 90% yield of a mixture of the endo,anti adduct 13 and endo,syn adduct 14 (77:23, estimated by ^{1}H NMR spectrum). The mixture was chromatographed on silica gel (400 g), and slow elution with a mixture (1:20) of ethyl acetate and hexane gave the endo,anti adduct, 5β,6,7,8β-tetrachloro-1α,4α,8aα,10aα-tetrahydro-1,4-methano-5,8-dimethoxymethanoanthracene-9,10-dione (**13**), mp 208–209 °C, on recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1660, 1600 cm^{-1}; UV λ_{max} (methanol) 268 nm (ϵ 6560), 320 (910), 400 (90); ^{1}H NMR (CDCl$_3$) δ 2.24 (2 H, AB q, $J_1 = J_2 = 7$ Hz), 3.6 (5 H, s), 3.68 (3 H, s), 3.92 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.8 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR (CDCl$_3$) δ 48.6, 52.0, 53.1, 57.1, 71.1, 77.7, 111.2, 129.1, 141.8, 167.9, 188.1. Anal. Calcd for $C_{18}H_{14}O_4Cl_4$: C, 49.57; H, 3.23. Found: C, 49.52; H, 3.17.

Further elution of the column with the same solvent mixture gave the endo,syn adduct, 5α,6,7,8α-tetrachloro-1α,4α,8aβ,10aβ-tetrahydro-1,4-methano-5,8-dimethoxymethanoanthracene-9,10-dione (**14**), mp 199–201 °C, after recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1660, 720 cm^{-1}; UV λ_{max} (methanol) 270 nm (ϵ 6250), 316 (1050), 400 (90); ^{1}H NMR (CDCl$_3$) δ 2.22 (2 H, br s), 3.44–3.46 (2 H, m), 3.53 (3 H, s), 3.64 (3 H, s), 4.04 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.8 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR (CDCl$_3$) δ 48.6, 52.1, 53.1, 56.6, 74.6, 77.5, 111.2, 128.8, 142.5, 167.3, 187.7. Anal. Calcd for $C_{18}H_{14}O_4Cl_4$: C, 49.57; H, 3.24. Found: C, 49.66; H, 3.25.

Irradiation of 13. *syn*-5,6,7,8-Tetrachloro-16,16-dimethoxyheptacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{2,6}.0^{7,11}]octadec-13-ene-3,10-dione (21). The adduct 13 (50 mg, 0.11 mmol) was dissolved in 5 mL of dry benzene and diluted to 125 mL with hexane, and the solution was irradiated for 2 h, with use of Pyrex filter. Removal of the solvent under vacuum gave a residual solid, which was chromatographed on silica gel (5 g). Elution with a mixture (1:10) of ethyl acetate and hexane gave 21 (35 mg, 70%), mp 180 °C, after recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1760 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.98 (2 H, AB q, $J_1 = J_2 = 10$ Hz), 3.01 (2 H, br s), 3.14 (2 H, s), 3.66 (3 H, s), 3.68 (3 H, s), 6.32 (2 H, br s); ^{13}C NMR (CDCl$_3$) δ 41.5, 44.8, 51.5, 51.9, 58.0, 69.8, 74.2, 75.4, 105.4, 136.5, 201.1. Anal. Calcd for $C_{18}H_{14}O_4Cl_4$: C, 49.57; H, 3.23. Found: C, 49.50; H, 3.19.

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Regioselective De-O-benzylation with Lewis Acids

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Simple and highly regioselective de-O-benzylations of poly-O-benzylated monosaccharides and polyols with Lewis acids ($SnCl_4$ and $TiCl_4$) were developed. Spectral studies on intermediate complexes showed that three appropriately situated metal chelating functional groups were necessary for the selective de-O-benzylation.

Benzyl protecting groups are widely used in organic chemistry, and various methods for benzylation and debenzylation have been reported.[1] In particular, the recent development of organotin-mediated regioselective O-