Polycyclic Hydroxyquinones. Part 22.[1] Diels–Alder Reaction with Chloro Derivatives of Anthracene-1,4,9,10-tetraone

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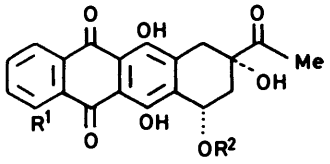
The Diels–Alder reaction of 2-chloro- and 2,3-dichloro-anthracene-1,4,9,10-tetraones (**8**) and (**9**) with substituted buta-1,3-dienes occurred at the internal double bond and gave angular adducts. The reaction of quinizarin (**4**) with chlorine in glacial acetic acid afforded the 2,3,4a,9a-tetrachloro-4a,9a-dihydroanthracene-1,4,9,10-tetraone (**17**). The cycloaddition of (**17**) with 2,3-dimethylbuta-1,3-diene (**10**) gave the fully aromatised linear adduct (**19**) whereas a reactive diene such as 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**12**) afforded the ketone (**22**), originating from the angular adduct. An explanation for the last result involves the ready halogen elimination in compound (**17**) to give (**9**) in the presence of a strongly nucleophilic diene.

The synthesis of anthracyclines, such as daunomycin (**1**), has been the subject of considerable interest in view of their application in the clinical treatment of a variety of cancers.[2] The fact that one of the structurally modified derivatives, the 4-demethoxydaunomycin (**2**), is even more effective than daunomycin (**1**) has simplified the regiochemical problems previously recognized.



(**1**) R^1 = OMe; R^2 = Daunosaminyl
(**2**) R^1 = H; R^2 = Daunosaminyl
(**3**) $R^1 = R^2$ = H

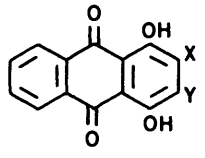
A retrosynthetic analysis shows that the corresponding aglycone, 4-demethoxydaunomycinone (**3**), could be constructed from a Diels–Alder reaction between the less stable tautomer of quinizarin (**4**), used as a BCD ring synthon, and a suitably substituted 1,3-diene. This reaction, however, requires rather drastic conditions and the cycloaddition product undergoes concomitant aromatization of the resulting A ring.[3]

Kende[4] and Lee[5] have used quinizarindiquinone [anthracene-1,4,9,10-tetraone (**7**)] as a BCD ring synthon. In this case, however, unless weakly activated dienes are used, cycloaddition occurs at the internal double bond of the diquinone, with the formation of angular adducts. The protection of the internal double bond of the diquinone has been proposed as a solution to this problem. Thus, Stoodley[6] prepared an epoxide which, even with electron-rich dienes, yielded linear adducts.

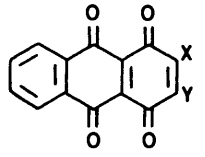
In previous studies[7] on the Diels–Alder reaction with substituted naphthazarins we have found that the introduction of chlorine atoms affected the regiochemistry of the cycloaddition with unsymmetrically substituted dienes and, in some cases, activated the quinone double bond. The presence of chlorine atoms on the external double bond of the quinizarindiquinone could perhaps favour the cycloaddition reaction, to yield linear adducts useful as key intermediates for syntheses of 4-demethoxydaunomycinone.

The present work reports our results on the preparation of chloro derivatives of quinizarindiquinone (**7**) and their cycloaddition reactions with various substituted dienes. We initially prepared the 2-chloroquinizarindiquinone (**8**) in 63% overall yield from quinizarin (**4**), using a reaction scheme involving the oxidation of (**4**) to the quinone (**7**), followed by the addition of hydrochloric acid to produce 2-chloroquinizarin (**5**), which was further oxidized to (**8**) upon treatment with lead tetra-acetate. The ^{1}H n.m.r. spectrum of compound (**8**) showed a multiplet at δ 8.1—7.6, corresponding to the four aromatic protons, and a singlet at δ 7.13 due to the quinonoid proton.

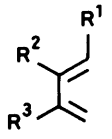
A similar sequence starting from 2-chloroquinizarin (**5**) produced 2,3-dichloroquinizarindiquinone (**9**) in 62% overall yield. However, this highly insoluble diquinone was too unstable to be fully characterized.



(**4**) X = Y = H
(**5**) X = Cl; Y = H
(**6**) X = Y = Cl



(**7**) X = Y = H
(**8**) X = Cl; Y = H
(**9**) X = Y = Cl



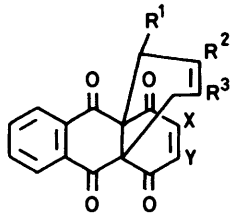
(**10**) R^1 = H; $R^2 = R^3$ = Me
(**11**) R^1 = $OSiMe_3$; $R^2 = R^3$ = H
(**12**) R^1 = OMe; R^2 = H; R^3 = $OSiMe_3$

The cycloaddition of 2-chloroquinizarindiquinone (**8**) with 2,3-dimethylbuta-1,3-diene (**10**) in dichloromethane at 0 °C afforded the adduct (**13**) which was isolated in 90% yield. The angular structure of the adduct was deduced from its ^{1}H n.m.r. spectrum which showed a signal at δ 6.8 assignable to the enedione olefinic proton vicinal to the chlorine. The mass spectrum displayed two retro Diels–Alder fragmentations at *m/z* 272 and 238, only compatible with the angular adduct. The

above assignment was further confirmed by the ^{13}C n.m.r. spectrum which showed four carbonyl carbon signals at δ 191.3, 190.6, 190.3, and 186.3. In addition, it also showed the C-2 and C-3 at δ 147.6 and 136.1 respectively and the quaternary carbon atoms in C-4a and C-9a at δ 65.1 and 65.8 respectively.

Essentially the same results were obtained by using a more electron-rich diene, such as the (*E*)-1-trimethylsilyloxybuta-1,3-diene (**11**). When the diquinone (**8**) reacted with the diene (**11**), in dichloromethane at −15 °C, the adduct (**15**) was isolated in 97% yield, presumably as a regioisomeric mixture (**15a**,**b**). The ^1H n.m.r. spectrum displayed a signal at δ 7.1 assignable to the enedione olefinic protons, and a broad singlet at δ 5.7 due to the 12-H and 13-H olefinic protons. The u.v.–vis spectrum was in accord with that of (**13**), whilst the mass spectrum showed two ionic fragments at *m/z* 298 and 272 which corresponded to two retro Diels–Alder fragmentations from the molecular ion. These observations clearly indicated a mixture consisting of (**15a** and **b**) both possessing the angular structure of (**15**).

The presence of two chlorine atoms on the external double bond of the diquinone does not modify these results. In fact, the reaction of 2,3-dichloroquinizarindiquinone (**9**) with 2,3-dimethylbuta-1,3-diene (**10**), in dichloromethane at 0 °C, afforded the internal cycloadduct (**14**) in 96% yield. Evidence in support of this structure was provided by the ^{13}C n.m.r. spectrum (see the Experimental section). Carbonyl carbon signals for compound (**14**) appeared at 190.2 and 184.1 p.p.m., while the C-2, C-3, C-4a, and C-9a also showed values consistent with those found for (**13**). In addition, the u.v.–vis and mass spectra agreed with those of compound (**13**). These



(**13**) X = Cl; Y = H; R^1 = H; R^2 = R^3 = Me

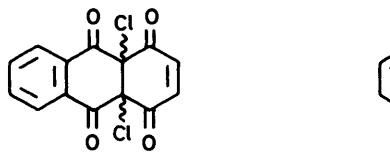
(**14**) X = Y = Cl; R^1 = H; R^2 = R^3 = Me

(**15**)**a**; X = Cl; Y = H; R^1 = $OSiMe_3$; R^2 = R^3 = H

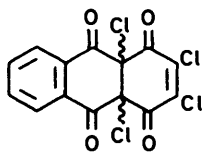
b; X = H; Y = Cl; R^1 = $OSiMe_3$; R^2 = R^3 = H

results show the angular nature of (**14**) and indicate that the presence of two chlorine atoms at positions 2 and 3 of the quinizarindiquinone does not enhance the reactivity of the external double bond towards the Diels–Alder reaction, although presumably a balance could exist between steric and electronic factors.[8]

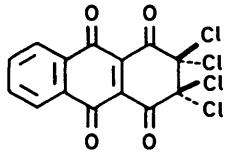
In view of the above results, we attempted to protect the internal double bond by halogen addition. A compound such as (**16**), with a protected internal double bond, appeared to be a suitable dienophile for our purpose. Some years ago, Sargent[9] described the preparation of the tetraone (**16**) from quinizarin (**4**) by treatment with chlorine in glacial acetic acid. The formation of (**16**) was interpreted as a prior oxidation to quinizarindiquinone, followed by chlorine addition. The reaction in our hands, under the aforementioned conditions, afforded a compound whose physical data coincided with those reported, but whose structure in fact corresponded to that of a tetrachloro derivative, as deduced from its elemental analysis consistent with a molecular formula $C_{14}H_4Cl_4O_4$. This conclusion was confirmed by the mass spectrum, which showed the molecular ion at *m/z* 376 (1.6%) and ionic fragments at *m/z* 341 (37%) and 306 (17.6) which correspond to (M^+ − Cl) and



(**16**)



(**17**)



(**18**)

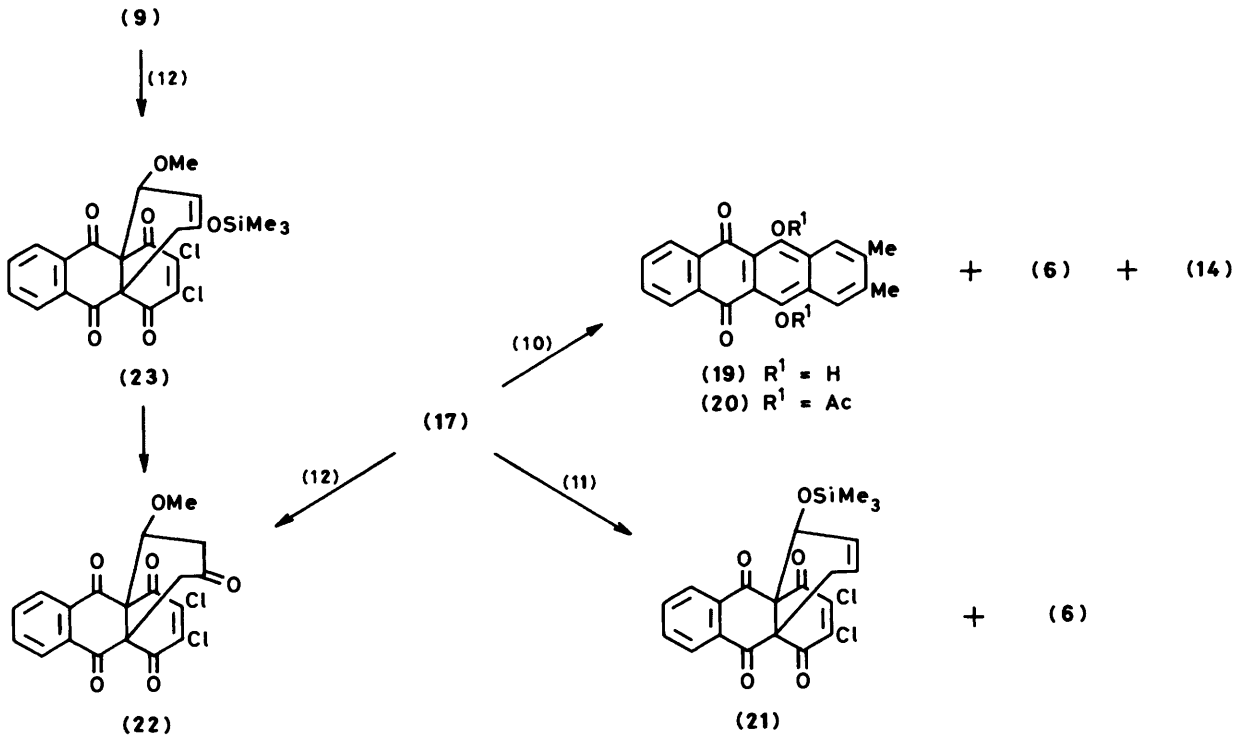
(M^+ − 2Cl), respectively. The ^1H n.m.r. spectrum showed only a multiplet at δ 8.0—8.3, assignable to the aromatic protons and there was no evidence of any signal that could be assigned to the enedione olefinic protons.

The above data are compatible with the structures of both (**17**) and (**18**) and the structural assignment was based on the ^{13}C n.m.r. spectrum of the product. The C-1/C-4 and C-9/C-10 carbonyl carbons appeared at 174.3 and 179.9 p.p.m., whereas C-2/C-3 and C-4a/C-9a appeared at 141.6 and 60.0. The estimated value for C-2/C-3 in (**17**) is 141.7 p.p.m., based on the ^{13}C shift of the 1,2-dichloroethene (δ 120.7) corrected for the effects of the α(+15) and α′(+6) CO groups. In the case of (**18**), however, the C-2 value should be closer to the 1,1,2,2-tetrachloroethane value of 74.2 p.p.m., corrected for the effects of vicinal CO groups. The absence of a naphthoquinone chromophore in the u.v.–vis spectrum and the presence in the i.r. spectrum of two carbonyl bands at 1 740 and 1 713 cm^{-1} further support the structure (**17**) for the compound.

The formation of compound (**17**) probably involves successive oxidation and chlorine addition. In fact, it has been shown that the reaction of 2,3-dichloroquinizarin (**6**) with chlorine, in glacial acetic acid, yields a product whose physical and spectral data coincide with those of (**17**).

Despite the fact that its structure differs from that described previously, compound (**17**) could be used in our projected synthesis, as it has the internal double bond in a protected form. The reaction of compound (**17**) with a simple diene, such as 2,3-dimethylbuta-1,3-diene (**10**), by refluxing in acetonitrile, gave a mixture of 2,3-dichloroquinizarin (**6**) (45%), the tetracyclic aromatic compound (**19**) (25%) and the angular adduct (**14**) (6%), which were separated by chromatography. The tetracyclic compound (**19**) was evidently produced by aromatization from the linear adduct and its structure was confirmed from the spectral data of its acetylated derivative (**20**), which coincide with those described previously.[3] The 2,3-dichloroquinizarin (**6**) was formed from the starting material (**17**) by halogen elimination and subsequent reduction. In fact, we have shown that compound (**17**), on refluxing in toluene or acetonitrile is converted into the quinizarin (**6**). The formation of the angular adduct (**14**) is justified because, under the given reaction conditions, chlorine could be eliminated to produce 2,3-dichloroquinizarindiquinone (**9**), which has been shown to react with the diene through the internal double bond.

In an attempt to produce the desired linear adduct, we used a more reactive diene, which would react under milder conditions. However, when the cycloaddition of (**17**) with (*E*)-1-trimethylsilyloxybuta-1,3-diene (**11**) was attempted at 0 °C, the reaction did not take place. Refluxing the reactants in acetonitrile produced 2,3-dichloroquinizarin (**6**) (18%) and the angular adduct (**21**) (56%). The angular nature of (**21**) was confirmed by comparison of its ^{13}C n.m.r. spectrum with those of the previously obtained angular adducts.



We have also attempted the cycloaddition under very mild conditions using a reactive diene, such as the Danishefsky diene (**12**). The tetraone (**17**) reacts with (*E*)-1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**12**), in dichloromethane at 0 °C, to afford in 70% yield, the ketone (**22**) originating from the angular adduct (**23**).

The structure (**22**) was assigned on the basis of its ^{13}C n.m.r. spectrum (see the Experimental section). The carbon atoms C-4a and C-9a appear at 68.2 and 65.3 p.p.m., whilst C-2 and C-3 resonate at 149.9 and 143.1 p.p.m. These data are in agreement with those for the angular adducts (**13**) and (**14**).

The structure (**22**) was also confirmed by an unequivocal synthesis from dichloroquinizarindiquinone (**9**). The reaction of (**9**) with the diene (**12**) gave the adduct (**23**), which by hydrolysis with hydrochloric acid in aqueous tetrahydrofuran, afforded the ketone (**22**). The physical and spectral data of the latter coincide with those of the compound produced from (**17**). Furthermore, its angular structure has been conclusively confirmed by *X*-ray crystallographic analysis.[10]

A reasonable explanation for the formation of the angular adduct by using such a reactive diene may be that in the presence of strongly nucleophilic alkenes, the elimination of chlorine in the tetrachloro derivatives (**17**) is favoured as a first step. Thus, it seems that the halogen elimination to give (**9**) and the cycloaddition to (**17**) are competing reactions. When strongly nucleophilic dienes are used, the halogen elimination is faster than the initial cycloaddition to (**17**), whereas with a weakly activated diene, the cycloaddition occurs preferentially. This explanation is supported by the fact that when the reaction of the tetraone (**17**) with 2,3-dimethylbuta-1,3-diene (**10**) was conducted at 25 °C, in the presence of ethyl vinyl ether, only the angular adduct (**14**) was isolated in 13% yield and no linear adduct was observed.

Experimental

Melting points are uncorrected. ^1H N.m.r. spectra were recorded on either a Hitachi Perkin-Elmer, R-24A (60 MHz) or a Bruker WM 200 SY (200 MHz) spectrometer for $CDCl_3$ solutions (unless otherwise stated). Chemical shifts are reported in p.p.m. (δ) downfield from Me_4Si. ^{13}C N.m.r. spectra were recorded on either a Varian XL/100 or a Bruker WM 200 SY spectrometer for $CDCl_3$ solutions (unless otherwise stated). I.r. spectra were obtained on a Pye Unicam SP-1100 spectrophotometer for Nujol mulls (unless otherwise stated). U.v.–vis spectra were determined on a Perkin-Elmer 124 instrument for ethanol solutions. Mass spectra were recorded on Hitachi Perkin-Elmer RMU-6MG or Hewlett Packard 5995A instruments. Analytical t.l.c. was performed on silica gel Merck G, deactivated by treatment with 0.05M-KH_2PO_4;[5] column chromatography was carried out on deactivated[5] (DGS) silica gel Merck 60 (70—230 mesh). Light petroleum refers to the fraction of boiling range 40—60 °C and ether refers to diethyl ether throughout.

2-*Chloro*-1,4-*dihydroxy*-9,10-*anthraquinone* (**5**).—The freshly prepared diquinone (**7**)[11] (4 g) was added to a mixture of glacial acetic acid (50 ml) and concentrated hydrochloric acid (50 ml). The reaction mixture was stirred at room temperature for 1 h and was then poured into ice–water (250 ml). The precipitated product was filtered and washed with water to give the quinone (**5**) (3.8 g, 83%), m.p. 242—243 °C (from chloroform–hexane) (lit.,[12] 239—240 °C).

2-*Chloroanthracene*-1,4,9,10-*tetraone* (**8**).—To a suspension of the quinone (**5**) (0.6 g) in glacial acetic acid (25 ml) was added lead tetra-acetate (1.8 g). The reaction mixture was stirred at room temperature until the red colour had disappeared (*ca.* 1 h). The solid which appeared was filtered off and washed with ether–light petroleum to give the diquinone (**8**) (0.5 g, 84%). A sample was recrystallised from nitrobenzene at 80 °C by the the addition of CS_2 to give the tetraone (**8**), m.p. 206—208 °C, δ 8.1—7.6 (m, 4 H) and 7.13 (s, 1 H).

2,3-*Dichloro*-1,4-*dihydroxy*-9,10-*anthraquinone* (**6**).—Recently prepared diquinone (**8**) (0.5 g) was added to a mixture of glacial acetic acid (25 ml) and concentrated hydrochloric acid (25 ml). The reaction mixture was stirred at room temper-

ature for 2 h, and was then poured into ice–water (100 ml). The precipitate was filtered and washed with water to give (**6**) (0.48 g, 83%), m.p. 249 °C (from acetone) (lit.,[9,13] 249.5—251 °C).

2,3-*Dichloroanthracene*-1,4,9,10-*tetraone*[14] (**9**).—To a suspension of the quinone (**6**) (0.3 g, 0.9 mmol) in glacial acetic acid (25 ml) was added lead tetra-acetate (0.6 g, 1.36 mmol). The reaction mixture was stirred at room temperature until the red colour had disappeared (*ca.* 1 h). The precipitate was filtered and washed with ether–light petroleum to give the diquinone (**9**) (0.28 g, 87%), m.p. 224—226 °C (from nitrobenzene at 80 °C by the addition of CS_2).

2-*Chloro*-12,13-*dimethyl*-4a,9a-*dihydro*-4a,9a-(*but*-2-*eno*)-*anthracene*-1,4,9,10-*tetraone* (**13**).—To a suspension of the diquinone (**8**) (0.5, 1.41 mmol) in dichloromethane (50 ml) was added 2,3-dimethylbuta-1,3-diene (**10**) (2 ml). The reaction mixture was stirred at 0 °C for 3 h, and was filtered through deactivated acid silica gel. The solvent was evaporated off under reduced pressure and the residue was triturated with ether and ether–light petroleum. The precipitate was filtered off and identified as the adduct (**13**) (0.65 g, 90%), m.p. 130—132 °C (Found: C, 67.6; H, 4.4; Cl, 9.7. $C_{20}H_{15}ClO_4$ requires C, 67.7; H, 4.3; Cl, 10.0%); *m/z* 354 (M^+), 272, 238, 133, and 104; $\nu_{max.}$ 1 735, 1 715, and 1 690 cm^{-1}; $\delta_H(CCl_4)$ 8.1—7.5 (m, 4 H), 6.8 (s, 1 H), 2.45 (br s, 4 H), and 1.6 (s, 6 H); δ_C 191.3, 190.6, 190.3, 186.3, 147.6, 136.1, 135.2, 135.0, 133.1, 132.6, 127.8, 122.4, 122.2, 65.8, 65.1, 33.2, and 18.5; $\lambda_{max.}$ 228, 254, and 307 nm (log ε 4.67, 4.42, and 2.51).

2-*Chloro*-11-*trimethylsilyloxy*-4a,9a-*dihydro*-4a,9a-(*but*-2-*eno*)*anthracene*-1,4,9,10-*tetraone* (**15**).—To a solution of the diquinone (**8**) (0.5 g, 1.2 mmol) in dichloromethane (50 ml) at −15 °C was added dropwise a solution of (*E*)-1-trimethylsilyloxybuta-1,3-diene (**11**) (0.35 g, 2.46 mmol) in dichloromethane (10 ml). The reaction mixture was stirred at −15 °C for 1 h. The solvent was removed under reduced pressure and the residue dissolved in benzene was precipitated by cyclohexane. The solid which appeared was filtered off and characterised as the adduct (**15**) (0.48 g, 97%), m.p. 154—156 °C (from heptane) (Found: C, 61.3; H, 4.8; Cl, 8.8. $C_{21}H_{19}ClO_5Si$ requires C, 60.8; H, 4.6; Cl, 8.5%); *m/z* 414 (M^+), 399, 379, 325, 298, and 272; $\nu_{max.}$ 1 720, 1 715, 1 695, and 1 685 cm^{-1}; δ_H 8.2—7.6 (m, 4 H), 7.1 (s, 1 H), 5.7 (br s, 2 H), 5.0 (m, 1 H), 3.4—1.8 (m, 2 H), and 0.05 (s, 9 H); $\lambda_{max.}$ 228, 253sh, and 312 nm (log ε 4.20, 3.92, and 3.04).

2,3-*Dichloro*-12,13-*dimethyl*-4a,9a-*dihydro*-4a,9a-(*but*-2-*eno*)-*anthracene*-1,4,9,10-*tetraone* (**14**).—To a solution of the diquinone (**9**) (0.5 g, 1.28 mmol) in dichloromethane (50 ml) at 0 °C was added 2,3-dimethylbuta-1,3-diene (**10**) (2 ml, 3.2 mmol). The reaction mixture was stirred for 2 h and filtered through deactivated acid silica gel. The solvent was removed under reduced pressure to give the adduct (**14**) (0.61 g, 96%), m.p. 177—178 °C (from ether-light petroleum) (Found: C, 61.3; H, 3.8; Cl, 17.8. $C_{20}H_{14}ClO_4$ requires C, 61.4; H, 4.1; Cl, 18.1%); *m/z* 388 (M^+), 373, 306, and 238; $\nu_{max.}$ 1 730, 1 720, and 1 692 cm^{-1}; δ_H 8.11—8.07 (m, 2 H), 7.84—7.79 (m, 2 H), 2.59 (m, 4 H), and 1.66 (s, 6 H); δ_C 190.2, 184.1, 144.4, 135.3, 132.7, 127.9, 122.2, 64.9, 33.5, 33.3, and 18.5; $\lambda_{max.}$ 228, 262, and 322 nm (log ε 4.51, 4.24, and 3.39).

2,3,4a,9a-*Tetrachloro*-4a,9a-*dihydroanthracene*-1,4,9,10-*tetraone* (**17**).—*Method A*. A gentle stream of chlorine was passed through a stirred suspension of quinizarin (**4**) (1 g) in glacial acetic acid (20 ml) at room temperature for 4 days. The precipitate was filtered and washed with water to give the tetraone (**17**) (0.76 g, 50%), m.p. 220 °C (from carbon tetrachloride) (lit.,[9] 218—220 °C) (Found: C, 44.5; H, 1.2; Cl, 36.9. $C_{14}H_4Cl_4O_4$ requires C, 44.7; H, 1.1; Cl, 37.2%); *m/z* 376 (M^+), 341, and 306; $\nu_{max.}$(KBr) 1 740 and 1 713 cm^{-1}; $\delta_H([^2H_6]Me_2SO)$ 8.0—8.3 (m, 4 H); δ_C 179.9, 174.3, 141.6, 136.0, 130.0, 128.6, and 60.0; $\lambda_{max.}$ 234, 267, and 315sh nm.

Method B. As above but starting with the quinone (**6**) (100 mg) to give the tetraone (**17**) (74 mg, 61%), m.p. 220 °C, identical with the sample prepared by method A above.

Reaction of the Tetraone (**17**) *with* 2,3-*Dimethylbuta*-1,3-*diene* (**10**).—A solution of compound (**17**) (308 mg, 0.8 mmol) and the diene (**10**) (2 ml) in dry acetonitrile (40 ml) and hydroquinone (50 mg) was refluxed for 24 h. After the reaction had been cooled, the solvent was removed in under reduced pressure and the crude residue was chromatographed on deactivated silica gel (DSG) using succesively, toluene–hexane (2:1) and toluene–hexane (1:2) as the eluants to give the quinone (**6**) (113 mg, 45%), the adduct (**14**) (10 mg, 6%), and 2,3-dimethyl-6,11-(or 5,12-)dihydroxynaphthacene-5,12-(or 6,11-)quinone (**19**) (35 mg, 25%), m.p. 318 °C (lit.,[3] 317 °C); $\nu_{max.}$ 1 612, 1 590, and 1 510 cm^{-1}; $\lambda_{max.}$(dioxane) 518, 484, 456, 429sh, and 308 nm (log ε 3.46, 3.63, 3.38, 3.04, and 4.50); *m/z* 318 (M^+), 303, 288, 261, 233, 159, and 144; δ_H 14.60 (s, 2 H), 8.41—8.36 (m, 2 H), 8.10 (s, 2 H), 7.75—7.70 (m, 2 H), and 2.40 (s, 6 H). To a solution of the quinone (**19**) (0.1 g) in acetic anhydride (5 ml) was added three drops of sulphuric acid. The reaction mixture was stirred at room temperature for 1 h and was then poured into a mixture of ice–water (100 ml). The precipitated product was filtered off and washed with water to give the 5,12-(or 6,11-)diacetoxy-2,3-dimethylnaphthacene-6,11-(or 5,12-)quinone (**20**) (0.1 g, 92%), m.p. 252—253 °C (from methanol) (lit.,[3] 248 °C), δ_H 8.25—8.15 (m, 2 H), 7.98 (m, 1 H), 7.88 (m, 6 H), 7.80—7.72 (m, 2 H), 2.67 (s, 3 H), 2.66 (s, 3 H), 2.50 (s, 3 H), and 2.40 (s, 3 H); $\lambda_{max.}$(dioxane) 285, 293, 396, 422sh, and 464sh nm (log ε 4.35, 4.36, 3.65, 3.30, and 3.19), *m/z* 402 (M^+), 360, 318, 303, 289, and 261.

2,3-*Dichloro*-11-*trimethylsilyloxy*-4a,9a-*dihydro*-4a,9a-(*but*-2-*eno*)*anthracene*-1,4,9,10-*tetraone* (**21**).—A solution of the tetraone (**17**) (0.5 g, 1.5 mmol) in dry acetonitrile and (*E*)-1-trimethylsilylxoybuta-1,3-diene (**11**) (0.35 g, 2.46 mmol) was heated at 50 °C for 24 h. After cooling, the solvent was removed under reduced pressure and the residue was triturated with ether and hexane to give the adduct (**21**) (0.41 g, 56%), m.p. 159—160 °C (from hexane) (Found: C, 56.3; H, 4.05; Cl, 15.1. $C_{21}H_{18}Cl_2O_5Si$ requires C, 56.25; H, 4.0; Cl, 15.6); *m/z* 448 (M^+), 433, 413, 316, 378, 360, 316, and 132; $\nu_{max.}$ 1 740, 1 720, and 1 692 cm^{-1}; δ_H 8.2—7.7 (m, 4 H), 5.9 (br s, 2 H), 5.1 (m, 1 H), 3.6—3.1 (m, 1 H), 2.4—1.9 (m, 1 H), and 0.0 (s, 9 H); δ_C 192.2, 188.1, 185.3, 182.0, 143.7, 135.9, 135.7, 135.2, 134.7, 131.1, 128.5, 127.9, 127.2, 125.6, 68.8, 66.0, 62.1, 26.8, and −0.3; $\lambda_{max.}$ 228, 262, and 314sh nm (log ε 4.27, 3.97, and 3.10). The ether and hexane were evaporated off from the mother liquor under reduced pressure and the residue was purified by chromatography eluting with benzene–hexane (1:1) to give the quinone (**6**) (0.09 g, 18%).

2,3-*Dichloro*-11-*methoxy*-13-*trimethylsilyloxy*-4a,9a-*dihydro*-4a,9a-(*but*-2-*eno*)*anthracene*-1,4,9,10-*tetraone* (**23**).—To a solution of the diquinone (**9**) (200 mg, 0.65 mmol) in dry dichloromethane (20 ml) at −10 °C was added a solution of (*E*)-1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**12**) (200 mg, 1.4 mmol) in dry dichloromethane (8 ml). The reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ether to give the adduct (**23**) (160 mg, 55%), m.p. 180—181 °C (from chloroform–hexane), $\nu_{max.}$ 1 740, 1 715, 1 695, and 1 670 cm^{-1}; δ_H 8.14—8.03 (m, 2 H), 7.88—7.75 (m, 2 H), 5.29 (dt, 1 H, *J* 5.6, 1.5 Hz), 4.79 (dd, 1 H, *J* 0.5, 5.6 Hz), 3.23 (dd, 1 H, *J* 18.5, 1.3 Hz),

3.17 (s, 3 H), 2.14 (m, 1 H), and 0.22 (s, 9 H); δ_C 191.6, 186.8, 184.3, 182.0, 151.1, 149.3, 143.4, 136.0, 135.2, 134.3, 130.8, 128.4, 128.0, 101.3, 75.2, 67.4, 63.2, 56.0, 30.6, and 0.1; *m/z* 478 (M^+), 442, 407, and 379.

2,3-*Dichloro*-11-*methoxy*-4a,9a-(*butano*)*anthracene*-1,4,9,10,13-*pentaone* (**22**).—*Method A*. To a stirred solution of the tetraone (**17**) (0.5 mg, 1.62 mmol) in dry dichloromethane (50 ml) at 0 °C was added the diene (**12**) (0.42 g). The mixture was allowed to react under these conditions for 24 h. The solvent was removed under reduced pressure to give a crude oil, which was triturated with ether to give the ketone (**22**) (0.37 g, 70%), m.p. 250—251 °C (from acetone–hexane) (Found: C, 56.0; H, 3.0; Cl, 16.7. $C_{20}H_{12}Cl_2O_6$ requires C, 56.15; H, 2.95; Cl, 17.2); *m/z* 406 (M^+), 371, 320, 308, 285, and 256; $\nu_{max.}$ 1 740, 1 710, and 1 685 cm^{-1}; δ_H 8.20—7.87 (m, 4 H), 4.68 (t, 1 H, *J* 3 Hz), 3.41 (dd, 1 H, *J* 15.6, 1.9 Hz), 3.21 (s, 3 H), 2.95 (m, 1 H), 2.80 (dd, 1 H, *J* 3.15, 16.2 Hz), and 2.38 (d, 1 H, *J* 15.3 Hz); δ_C 199.3, 189.5, 187.9, 183.3, 180.9, 149.9, 143.1, 136.4, 135.9, 134.0, 130.7, 128.9, 128.1, 81.5, 68.2, 65.3, 57.3, and 41.4; $\lambda_{max.}$ 230, 262, and 315sh nm (log ε 4.5, 4.2, and 3.3).

Method B. A solution of the adduct (**23**) (380 ml) in 3% hydrochloric acid in THF–water (9:1; 15 ml) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure to give a crude oil which was triturated with ether to give the ketone (**22**) (250 mg, 80%), m.p. 250—251 °C (from acetone–hexane) identical with the product described above.

Reaction of the Tetraone (**17**) *with the Diene* (**10**) *in the Presence of Ethyl Vinyl Ether*.—To a solution of the tetraone (**17**) (113 mg) in dry acetonitrile (15 ml) was added 2,3-dimethylbuta-1,3-diene (**10**) (1 ml) and ethyl vinyl ether (22 mg). The reaction mixture was stirred at room temperature for 3 days. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel (DSG) using toluene–hexane (2:1) as the eluant to give the quinone (**6**) (12 mg, 15%) and the adduct (**14**) (13 mg, 13%) identical with the products described above.

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