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REACTIONS OF KETENE ACETALS—14[1]

THE USE OF SIMPLE MIXED VINYLKETENE ACETALS IN THE ANNULATION OF QUINONES

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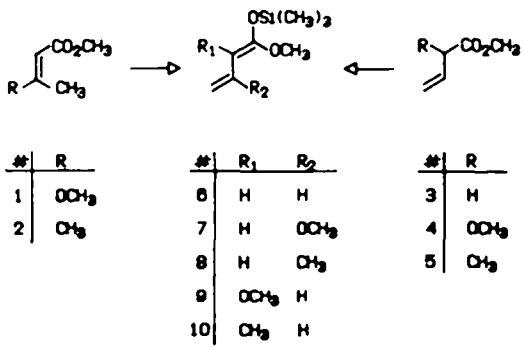
Abstract —α, β- and β, γ-unsaturated esters can be converted by strong base and chlorotrimethylsilane to the corresponding mixed vinylketene acetals which are shown to be particularly useful and generally applicable reagents for the regiospecific annulation of halogenoquinones. The reaction proceeds readily with a variety of substrates including benzoquinones.

Recently various vinylketene acetals had been shown to be convenient partners with halogenated quinones in the regiospecific synthesis of a number of naturally occurring substances.[2] In a preliminary communication,[3] a simple and general procedure was proposed using readily available unsaturated esters to generate the diverse dienes required for the efficient elaboration of the great variety of substitution patterns encountered. The usefulness of the method has been attested since then by the frequency with which it has been applied.[4]

Preparation of dienes. Although formation of a dienolate ion by the action of strong base on an unsaturated ester and its conversion to a mixed vinylketene acetal by quenching with a chlorosilane had briefly been alluded to earlier,[5] preparation of these dienes did not become common practice until 1979.[3,4,6] Many bases such as lithium cyclohexylisopropylamide[7] or 2, 2, 6, 6-tetramethylpiperidide[8] and sodium or lithium bistrimethylsilylamide[9] have been suggested for such purposes, but Ainsworth's[10] basic procedure as devised for more simple systems, using lithium diisopropylamide, was found overall to be the most satisfactory. In the few cases examined, sodium bistrimethylsilylamide gave comparable yields, however it was found to be much less convenient to handle. The other bases were indeed as effective but they tended to give products contaminated with the liberated amine which was not the case when LDA was chosen (Scheme 1).

Various attempts to establish the best reaction conditions are summarized in Table 1. This shows clearly that distillation of the diene at the lowest possible temperature is the sole most important factor affecting yield and confirms the ease with which these compounds undergo thermal rearrangement.[11] It also indicates that a fairly slow addition of the chlorosilane at −78°, preferably diluted in solvent and followed by a gradual return to room temperature also tends to improve the overall process.



#	R
1	OCH_3
2	CH_3

#	R_1	R_2
6	H	H
7	H	OCH_3
8	H	CH_3
9	OCH_3	H
10	CH_3	H

#	R
3	H
4	OCH_3
5	CH_3

Scheme 1.

Among simple dienes, the 3-Me- and 3-OMe-derivatives are obtained straightforwardly from the corresponding α, β-unsaturated methyl esters in good to high yields. These compounds are the most stable of the series and can be kept for several weeks in a freezer without apparent deterioration. Routine examination (90 MHz NMR etc) seems to indicate that the products are homogeneous but since originally prepared diene **8** has been described as a 1 : 1 mixture of isomers[11b] on the basis of a 200 MHz NMR spectrum.

Mixed vinylketene acetals, unsubstituted on the 3-position are also accessible in principle from α, β-unsaturated esters if HMPA is incorporated to the reaction medium in order to preclude Michael-type additions to the unreacted substrate.[12] In view of the many disadvantages of handling HMPA, it was eventually judged more advantageous to use the equally accessible β, γ- unsaturated analogs which, laking conjugation, did not require use of the additive.

Starting materials were either commercial products or available by standard methods. Methyl 3-butenoate was prepared conveniently albeit in low yield by the acid catalyzed methanolysis of allyl cyanide while a Reformatsky reaction between methyl chloroformate and crotyl bromide provided a quite acceptable yield of methyl 2-methyl-3-butenoate.[13] Finally the cyanohydrin of acrolein after methanolysis and etherification with methyl iodide and silver (I) oxide afforded methyl 2-methoxy-3-butenoate.[14]

Reactions with halogenated quinones. Cycloadditions of vinylketene mixed acetals with quinones were systematically conducted in benzene at room temperature. An earlier procedure using THF at low temperatures was discarded although it generally gave slightly higher yields since it also produced a variety of troublesome by-products. Aromatization could be achieved either through pyrolysis of the neat

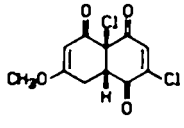
Table 1. Effect of various parameters on yield of diene 7

Nature and ratio of base to substrate	Reaction Time (min)	Addition Time (ClTMS) (min)	Distillation Pressure (mm Hg)	Yield %
LDA 1:1	10	5	15	50[a]
LDA 2:1	30	6	15	49
LDA 2:1	30	3	15	44
LDA[b] 1:1	40	15[c]	0.5	71
LDA 1:1	30	75[c]	0.4	71
LDA 1:1	60	180[c]	17	54
LICA 1:1	15	15	23	~ 50[ad]
LICA 1:1	30	5	15	~ 50[d]
LTMP 1:1	30	5	7	48[d]

a) Some unreacted material b) Inverse addition c) ClTMS diluted with equal volume of THF d) contaminated with amine.

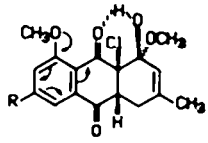
adduct at the appropriate temperature (when evolution of hydrogen halide is detected) or better by slow percolation of the reaction mixture through a column of silica gel. Thus pyrolysis of an adduct obtained from quinone **11** and diene **8** gave **18a** and **18b** with yields of 52% and 13% while aromatization on silica gel increased these to 76% and 14% respectively. In the anthraquinone series the difference was even more marked, pachybasin (**37a**) being produced from **29** and **8** by the thermal process in a yield of only 26% (+ 7% of **37b**) which was improved to 92% (+ 3% of **37b**) by contact with active adsorbent.

Reactions involving mixed vinylketene acetals obviously can give two quinonic products depending upon which oxygenated function is eliminated during aromatization. In fact only small amounts (less than 5%) of the O-Me derivative were usually encountered, a surprising chemoselective result which nonetheless indicates that a rapid acid-catalyzed rupture of the silyl ether is taking place followed by ketonisation and highly selective loss of the OMe group. In one instance, a 15% yield of such an intermediate **19c** was in fact encountered and surprisingly found to



19c

be rather resistant to aromatization. Condensation with 3-chloro-5-methoxynaphthoquinones behaved somewhat differently giving much higher proportions of the methyl ether (up to 44%). This observation can tentatively be ascribed to a well established increase of the electron density on the oxygen of the 10-CO and the resultant stabilization of the intermediate hemiacetal **i** through more effective H- bonding and eventually a greater competition between the two oxygenated function during elimination.

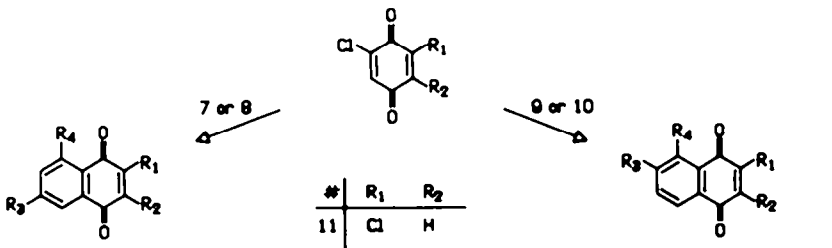


i

The behavior of mixed vinylketene acetals towards benzoquinones in contrast to that of the analogs used previously[15] gave unexpectedly good results and thus for the first time allowed truly advantageous preparations of naphthoquinones to be carried out by this approach. This difference seems to be related to a decreased reactivity with respect to less hindered dialkoxydienes since yields were not appreciably improved by lowering reaction temperatures (Scheme 2).

The dichloro derivatives **11** and **12** in particular yield various intermediates invaluable for the subsequent synthesis of anthraquinones while the 2-chloro-5- and 6-methoxy analogs **13** and **14** provide convenient access to the natural products 3-methoxy-7-methyljuglone **21a** and flaviolin-2, 7-dimethyl ether **22a** in conjunction with the appropriate diene (**8** or **7**). More complex substances such as a trimethyl ether of spinochrome B (**23**) or an isomer (**28a**) of diomelquinone A (converted to the natural product 6-O-methyldiomelquinone A), can be obtained directly from the simple substrates **15** or **16** and the dienes **7** or **9**.

Halogenated naphthoquinones also combine with



#	R_1	R_2
11	Cl	H
12	H	Cl
13	OCH_3	H
14	H	OCH_3
15	OCH_3	OCH_3
16	H	CH_3

#	R_1	R_2	R_3	R_4
17a	Cl	H	OCH_3	OH
17b	Cl	H	OCH_3	OCH_3
18a	Cl	H	CH_3	OH
18b	Cl	H	CH_3	OCH_3
19a	H	Cl	OCH_3	OH
19b	H	Cl	OCH_3	OCH_3
20a	H	Cl	CH_3	OH
20b	H	Cl	CH_3	OCH_3
21a	OCH_3	H	CH_3	OH
22a	H	OCH_3	OCH_3	OH
22b	H	OCH_3	OCH_3	OCH_3
23a	OCH_3	OCH_3	OCH_3	OH

#	R_1	R_2	R_3	R_4
24a	Cl	H	OCH_3	OH
25a	Cl	H	CH_3	OH
25b	Cl	H	CH_3	OCH_3
26a	H	Cl	OCH_3	OH
27a	H	Cl	CH_3	OH
27b	H	Cl	CH_3	OCH_3
28a	H	CH_3	OCH_3	OH
28b	H	CH_3	OCH_3	OCH_3

Scheme 2.

mixed vinylketene acetals giving convenient access in principle to a multitude of variously substituted anthraquinones. These substrates as expected are less reactive than the benzoquinones and cycloadditions are best conducted as suspensions or even in the absence of solvent. No exceptions were found and yields throughout vary from fair to excellent. In this study the usefulness of the process was examined by stressing the particular advantages of this approach.

The method was applied to the preparation of some simple but less readily available natural substances now accessible from unsaturated esters and the naphthoquinones obtained above. Thus chrysophanol (**39a**), isochrysophanol (**42a**) and 3-methoxychrysazin (**36a**) could all be obtained in one step from 3-chlorojuglone (**31**). Chloronaphthazarin (**33**) provided a simple synthesis of helminthosporin (**40a**) while recently prepared more complex naphthoquinones **26a**, **27a** and **34** gave derivatives (**44** and **46**) of morindone and copareolatin.

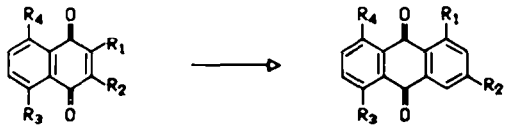
The well established regiospecificity[2a] of such reactions is retained in the case of mixed vinylketene acetals and can be strikingly illustrated by the synthesis of chrysophanol (**39a**) and ziganein (**38a**) from diene **8** and isomeric chlorojuglones **31** and **30** as well as by those of isochrysophanol (**42a**) and "iso-ziganein" (**41a**) from diene **10** and the same pair of substrates.

Directing the regiochemistry of cycloaddition with halogen substituents has long been known to allow a convergent approach[15] to the synthesis of anthraquinones. The unsatisfactory behaviour of diene **6** was established in the preparation of chrysophanol (**39a**) in 17% yield from naphthoquinone **18a** whereas from 3-chlorojuglone (**31**) and diene **8** a 63% conversion could be obtained. Similarly morindone 6-methyl ether (**44**) was accessible from both naphthoquinone **26a** and **27a**. The approach with the latter is far more satisfactory (63% instead of 17% from **26a**) since it uses the more efficient diene **9** although substrate **26a** is obtained in better yield than **27a** thus partially nullifying the advantage. A final example involves the preparation of physcion (**47a**). The procedures from **17a** or **18a** and the appropriate diene are comparable (63% and 68% respectively) and since the substrates **17a** and **18a** can both be obtained in good yield neither is clearly preferable.

The direct synthesis of a specific partially methylated polyhydroxyanthraquinone by using the appropriate choice of available dienes has already been pointed out.[16] Mixed vinylketene acetals provide yet another such reagent and considerably extends the scope of this approach. For instance quinone **32** and diene **8** give chrysophanol 8-methyl ether (**39c**) while, the 1-methyl ether **39b** is accessible as a by-product of the reaction between **18a** and diene **6**. Finally the isomeric "emodin 6, 8-" (**47b**) and "1, 6-dimethyl ethers" (**47c**) can be obtained readily from **17b** and **18b** respectively.

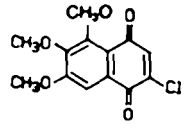
The usual regiochemistry dependent only on the position of the halogen was observed throughout with one minor but significant exception. 5, 7-Dimethoxy-3-chloronaphthoquinone (**17b**) in which the electronic effects of the OMe groups oppose an attack on the unsubstituted position gave 2 6% of a product **48** corresponding to an ipso-attack of the nucleophilic end of the diene on the Cl-bearing site. This is the first and only exception encountered so far and is of interest since it pinpoints the situation in which the regiospecificity begins to break down.

With a particular type of substrate, 3-chlorojuglone (**31**), another type of product was also de-



#	R_1	R_2	R_3	R_4
29	Cl	H	H	H
30	H	Cl	H	OH
31	Cl	H	H	OH
32	Cl	H	H	OCH_3
33	Cl	H	OH	OH

#	R_1	R_2	R_3	R_4
35a	OH	OCH_3	H	H
36a	OH	OCH_3	H	OH
36b	OCH_3	OCH_3	H	OCH_3
37a	OH	CH_3	H	H
37b	OCH_3	CH_3	H	H
38a	OH	CH_3	OH	H
39a	OH	CH_3	H	OH
39b	OCH_3	CH_3	H	OH
39c	OH	CH_3	H	OCH_3
39d	OCH_3	CH_3	H	OCH_3
40a	OH	CH_3	OH	OH
40b	OCH_3	CH_3	OH	OH



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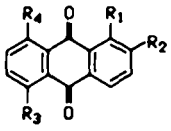
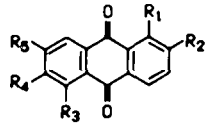
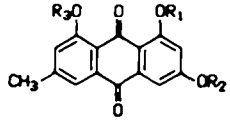


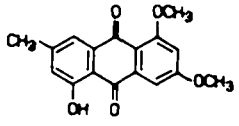


#	R_1	R_2	R_3	R_4
41a	OH	CH_3	OH	H
41b	OCH_3	CH_3	OH	H
42a	OH	CH_3	H	OH
42b	OCH_3	CH_3	H	OH

#	R_1	R_2	R_3	R_4	R_5
43a	OH	OCH_3	H	H	H
43b	OCH_3	OCH_3	H	H	H
44a	OH	OCH_3	OH	CH_3	H
44b	OCH_3	OCH_3	OH	CH_3	H
44c	OCH_3	OCH_3	OCH_3	CH_3	H
45a	OH	CH_3	H	H	H
45b	OCH_3	CH_3	H	H	H
46a	OH	CH_3	OCH_3	OCH_3	OCH_3
46b	OCH_3	CH_3	OCH_3	OCH_3	OCH_3



#	R_1	R_2	R_3
47a	H	CH_3	H
47b	CH_3	CH_3	H
47c	H	CH_3	CH_3
47d	CH_3	CH_3	CH_3



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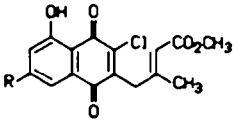
Scheme 3.

tected. These substances easily identified from the spectral data as γ-quinonylcrotonic esters ii may be present in other reaction mixtures where they constitute less than 1% of the products but are significantly more abundant (5–14%) in the specified cases. The occurence of these compounds is undoubtedly important from the mechanistic point of view but at present it is uncertain whether they arise along with cycloadducts from a common intermediate or as the result of a side-reaction. In any event, the formation of such substances appears to be favored when "internal acid catalysis" is present, i.e. in juglones and accentuates the polar aspect of the process.



ii

EXPERIMENTAL

All m.ps were taken for samples in capillary tubes with a Thomas-Hoover Apparatus and are not corrected. The UV and IR spectra were determined on Hewlett-Packard 8450A and Beckman Model IR-12 or IR-4250 spectrophotometers. NMR spectra were recorded with Bruker HX-90 or when indicated Varian EM-360A (60 MHz) spectrometers using TMS as an internal standard. Mass spectra were obtained with Varian M-66 or Hewlett-Packard 5995A GC/MS spectrometers. Woelm silica gel, activity III, or Merck silica gel $60F_{254}$, both for dry column chromatography, were used throughout in a product to adsorbent ratio of 1:50–100. Identification of synthetic compounds with authentic materials was carried out by TLC in at least four solvent systems and by comparison of their spectra. Elemental analyses were provided by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of unsaturated esters

Methyl (E)-3-*methoxy*-2-*butenoate* (**1**). This compound was obtained in 95% yield according to the method described for the ethyl ester,[17] b.p. 128–132°/200–250 mm (lit.[18] b.p. 175–177°); IR ν_{max} (film) 2960, 2820, 1712, 1630, 1430, 1390, 1360, 1285, 1190, 1140 and 1050 cm^{-1}; NMR ($CDCl_3$) δ 2.28 (3H, s, 4-H), 3.63, 3.64 (2 × 3H, 2s, 1, 3-OCH_3) and 5.03 (1H, br s, 2-H).

Methyl 3-*butenoate* (**3**) was produced conveniently but in low yield (23%) by the acid-catalyzed methanolysis of allyl cyanide, b.p. 107–109°.

Methyl 2-*methoxy*-3-*butenoate* (**4**). This ester was prepared from the corresponding 2-hydroxy compound[14] using silver (I) oxide and methyl iodide (87%), b.p. 63–64°/24 mm; IR ν_{max} (film) 2945, 2820, 1753, 1640, 1435, 1275, 1200, 1135, 1105, 1010, 990, 935 and 755 cm^{-1}; NMR ($CDCl_3$) δ 3.36 (3H, s, 2-OCH_3), 3.76 (3H, s, 1-OCH_3), 4.20 (1H, ddd, J = 6.0, 1.3, 1.0 Hz, 2-H), 5.24 (1H, ddd, J = 9.5, 2.0, 1.3 Hz, 4-H), 5.35 (1H, ddd, J = 16.5, 2.0, 1.0 Hz, 4-H), 5.79 (1H, ddd, J = 16.5, 9.5, 6.0 Hz, 3-H); mass spectrum: *m/e*, 130 (M^+). (Found: C, 55.16; H, 7.73. Calc for $C_6H_{10}O_3$: C, 55.37; H, 7.75%).

Methyl 2-*methyl*-3-*butenoate* (**5**). A Reformatsky reaction analogous to one used for the ethyl ester[13] gave a 60% yield of the methyl derivative, b.p. 117°/759 mm; IR ν_{max} (film) 1738, 1643, 1460, 1437, 1253, 1202 and 1162 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (3H, d, J = 7.0 Hz, 2-CH_3), 2.94 3.29 (1H, m, 2-H), 3.64 (3H, s, 1-OCH_3), 4.93 5.19 (2H, m, 4-H) and 5.85 (1H, ddd, J = 17.0, 10.0, 7.0 Hz, 3-H); mass spectrum: *m/e* 114 (M^+). (Found: C, 62.95; H, 8.99. Calc for $C_6H_{10}O_2$: C, 63.13; H, 8.83%).

Preparation of vinylketene acetals

General procedure. To a soln of LDA (105 mmols) in dry THF (100 mL) prepared in the usual way, then cooled to −78°, was added the unsaturated ester (100 mmols) over a period of 30 min. After 30–60 min, chlorotrimethylsilane (15 mL; ~120 mmols) in THF (10–25 mL) was introduced at the same temp and the medium allowed to reach room temp slowly (~1½ h). The solvent was then evaporated under vacuum, replaced by pentane, filtered and concentrated. Distillation of the residue gave the corresponding diene.

1-*Methoxy*-1-*trimethylsiloxy*-1,3-*butadiene* (**6**). The foregoing procedure applied to **3** gave diene **6** (68%), b.p. 32–35°/0.6 mm; IR ν_{max} (film) 1655, 1605, 1260, 1220, and 850 cm^{-1}; NMR ($CDCl_3$) δ 0.20, 0.24 (2s, 1-OTMS), 3.44 (s, 1-OCH_3), 4.11–4.80 (m, 2, 4-H) and 6.05–6.52 (m, 3-H). (Found: C, 55.83; H, 9.15; Si, 16.22. Calc for $C_8H_{16}O_2Si$: C, 55.76; H, 9.36; Si, 16.30%).

1, 3-*Dimethoxy*-1-*trimethylsiloxy*-1, 3-*butadiene* (**7**). Enolsilylation of **1** gave a 64% yield of the acetal **7**, b.p. 54–56°/0.5 mm; IR ν_{max} (film) 1660, 1270, 1255 and 845 cm^{-1}; NMR ($CDCl_3$) δ 0.24 (9H, s, 1-OTMS), 3.54 and 3.55 (2 × 3H, 2s, 1, 3-OCH_3), 3.98 (1H, dd, J = 1.5, 1.5 Hz, 4-H), 4.03 (1H, d, J = 1, 5 Hz, 4-H) and 4.33 (1H, d, J = 1.5 Hz, 2-H). (Found: C, 53.22; H, 9.09; Si, 14.02. Calc for $C_9H_{18}O_3Si$: C, 53.43; H, 8.96; Si, 13.88%).

1-*Methoxy*-3-*methyl*-1-*trimethylsiloxy*-1, 3-*butadiene* (**8**). Preparation of diene **8** from **2** was carried out in 71% yield, b.p. 35–40°/0.4 mm; IR ν_{max} (film) 1663, 1620, 1445, 1375 and 1260 cm^{-1}; NMR ($CDCl_3$) δ 0.21 (9H, s, 1-OTMS), 1.91 (3H, m, 3-CH_3), 3.51 (3H, s, 1-OCH_3), 4.24 (1H, br s, 2-H), 4.50 (1H, m, 4-H) and 4.74 (1H, m, 4-H). (Found: C, 58.17; H, 9.76; Si, 14.89. Calc for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74; Si, 15.07%).

1, 2-*Dimethoxy*-1-*trimethylsiloxy*-1, 3-*butadiene* (**9**). Diene **9** was prepared as a mixture of isomers in 63% yield from **4**, b.p. 36–70°/0.3 mm; IR ν_{max} (film) 1655, 1240, 1110, 865 and 845 cm^{-1}; NMR ($CDCl_3$) δ 0.26 and 0.28 (2s, 1-OTMS), 3.52, 3.57, 3.58 and 3.73 (4s, 1, 2-OCH_3), 4.72–4.95 (m, 4-H), 5.09 and 5.15 (2dd, J = 17.0, 2.0 Hz, 4-H), 6.34 and 6.46 (2dd, J = 17.0, 11.0 and 16.5, 11.0 Hz, 3-H).

1-*Methoxy*-2-*methyl*-1-*trimethylsiloxy*-1, 3-*butadiene* (**10**). The diene was obtained from **5** in a somewhat impure state (38%) as a 4:1 mixture of isomers, b.p. 58°/10 mm; IR ν_{max} (film) 1655, 1289, 1251, 1171, 1125, 860 and 845 cm^{-1}; NMR ($CDCl_3$) δ 0.14 (s, 1-OTMS), 1.63 (s, 2-CH_3), 3.46 (s, 1-OMe), 4.63 (dd, J = 10.0, 1.5 Hz, 4-H), 4.70 (dd, J = 17.0, 1.5 Hz, 4-H) and 6.42 (dd, J = 17.0, 10.0 Hz, 3-H) and ~0.14 (s, 1-OTMS), ~1.63 (s, 2-CH_3), ~3.46 (s, 1-OMe), 4.97 (dd, J = 10.0, 1.5 Hz, 4-H), 5.19 (dd, J = 17.0, 1.5 Hz, 4-H) and 6.58 (dd, J = 17.0, 10.0 Hz, 3-H).

Reactions of dienes with haloquinones

Method A. To a mixture of the haloquinone (1 mmol) in dry benzene (2 mL) was added (~1 min) the diene (1.2–2.0 mmol) in the same solvent (1 mL). The reaction was monitored by TLC and additional diene added as required. The mixture was adsorbed on silica gel (~60 g) and separated by elution with CCl_4 and/or a mixture of benzene and CCl_4 (1:1).

Method B. A soln of the diene (1 mmol) in dry THF (2 mL) was added dropwise to the haloquinone (1 mmol) in the same solvent (9 mL) at −30°. The mixture was stirred for 30 min, then allowed to warm to ambient temp (~1 hr) and evaporated. The crude product was treated as above using benzene as eluent.

Method C. The reaction was conducted as for method A in THF (1–2 mL) at room temp.

Method D. The quinone (1 mmol) was added to the diene (2 mmol) without solvent at room temp. Upon ascertaining that the reaction was complete, the mixture was adsorbed on silica gel and eluted with benzene.

3-*Chloro*-5-*hydroxy*-7-*methoxynaphthoquinone* (**17a**) *and its* 5-*methyl ether* **17b**. The condensation of **11** and diene **7**

(method B), after chromatography (CH_2Cl_2–pentane 1:1), gave **17a** (93%), identical to a previously prepared sample, m.p. 177° (ligroin) (lit.[15b] m.p. 177–178°); IR ν_{max} (KBr) 1657, 1633, 1593 and 1263 cm^{-1}; UV λ_{max} (EtOH) 271, 287 (sh) and 434 nm (log ϵ 3.54, 3.40 and 3.09); mass spectrum: *m/e* 238/240 (M^+). Elution with a 10:1 mixture of benzene and EtOAc provided **17b** (6%), also identical to an authentic sample, m.p. 205–207° (lit.[15b] 208–209°); IR ν_{max} (KBr) 1660, 1610, 1590, 1330 and 1210 cm^{-1}; UV λ_{max} (EtOH) 267, 293 and 360 nm (log ϵ 4.04, 4.03 and 3.52); mass spectrum: *m/e* 252/254 (M^+).

3-Chloro-5-hydroxy-7-methylnaphthoquinone (**18a**) *and the 5-methyl ether* **18b**. Chromatography (benzene) of the mixture obtained from an analogous reaction (method B) between **11** and diene **8** afforded **18a** (76%), m.p. 190–191° (petroleum ether, b.p. 65–110°) (lit.[19] m.p. 193–194°); IR ν_{max} (KBr) 1661, 1640, 1595 and 1263 cm^{-1}; UV λ_{max}(EtOH) 254, 263, 277, 369 and 428 nm (log ϵ 3.87, 3.91, 4.01, 2.78 and 3.52); NMR ($CDCl_3$) δ 2.44 (3H, s, 7-CH_3), 7.10 (1H, d, J = 1.0 Hz, 6-H), 7.16 (1H, s, 2-H), 7.46 (1H, d, J = 1.0 Hz, 8-H) and 11.64 (1H, s, 5-OH); mass spectrum: *m/e* 222/224 (M^+). (Found: C, 59.40; H, 3.23; Cl, 15.64. Calc for $C_{11}H_7ClO_3$: C, 59.34; H, 3.17; Cl, 15.93%).

A second zone (benzene–EtOAc 10:1) consisted of **18b** (14%), m.p. 174.5–175.5° (petroleum ether, b.p. 90–120°); IR ν_{max} (KBr) 1678, 1660, 1600 and 1335 cm^{-1}; UV λ_{max} (EtOH) 254, 265, 273, 340 and 410 nm (log ϵ 3.97, 3.99, 4.00, 2.91 and 3.44); NMR ($CDCl_3$) δ 2.48 (3H, s, 7-CH_3), 4.00 (3H, s, 5-OCH_3), 7.11 (2H, br s, 2, 6-H) and 7.54 (1H, d, J = 1.0 Hz, 8-H); mass spectrum: *m/e* 236/238 (M^+).

2-Chloro-5-hydroxy-7-methoxynaphthoquinone (**19a**) *and its 5-methyl ether* **19b**

(a) Reactions between **12** and diene **7** (method A) gave mixtures containing the ketonized adduct **19c** (15%) which could be isolated by precipitating it from a benzene solution by careful addition of petroleum ether, m.p. 150° (dec); IR ν_{max} (KBr) 1700, 1665, 1608, 1595, 1390, 1210 and 1184 cm^{-1}; NMR (CD_2Cl_2) δ 3.07 (1H, ddd, J = 18.0, 4.8, 1.5 Hz, 8-H), 3.27 (1H, dd, J = 18.0, 2.7 Hz, 8-H), 3.62 (1H, dd, J = 4.8, 2.7 Hz, 8a–H), 3.77 (3H, s, 7-OCH_3), 5.32 (1H, d, J = 1.5 Hz, 6-H) and 7.21 (1H, s, 3-H); mass spectrum: *m/e* 274/276 (M^+). Concentration of the filtrate and purification by chromatography (benzene–EtOAc 50:1) gave **19a** (42%), m.p. 162–163° (benzene–petroleum ether, b.p. 90–120°); IR ν_{max} (KBr) 1683, 1630, 1603, 1578 and 1275 cm^{-1}; UV λ_{max} (EtOH) 270, 286 and 438 nm (log ϵ 4.04, 3.86 and 3.60); NMR ($CDCl_3$) δ 3.63 (3H, s, 7-OCH_3), 6.73 (1H, d, J = 2.0 Hz, 6-H), 7.17 (1H, s, 3-H), 7.27 (1H, d, J = 2.0 Hz, 8-H) and 12.08 (1H, s, 5-OH); mass spectrum: *m/e* 238/240 (M^+).

(b) The crude product from a similar reaction was treated with excess MeI–Ag_2O and after chromatography (benzene–EtOAc 10:1) yielded **19b** (20%), m.p. 185–187° (lit.[15a] m.p. 187.5–188.5°) identical to a previously prepared sample; IR ν_{max} (KBr) 1675, 1650, 1612, 1590, 1552 and 1263 cm^{-1}; UV λ_{max} (EtOH) 270, 285 and 424 nm (log ϵ 3.99, 3.81 and 3.44); mass spectrum: *m/e* 252/254 (M^+).

2-Chloro-5-hydroxy-7-methylnaphthoquinone (**20a**) *and its 5-methyl ether* **20b**

(a) Compound C **20a** is the only product obtained from a reaction of **12** with diene **8** (method A), after separation by chromatography (benzene-EtOAc 50:1) (55%), m.p. 121–122° (EtOH) (lit.[19] m.p. 105°); IR ν_{max} (KBr) 1678, 1633, 1370 and 1260 cm^{-1}; UV λ_{max} (EtOH) 254, 262, 278 and 434 nm (log ϵ 3.95, 3.96, 4.06 and 3.63); NMR ($CDCl_3$) δ 2.42 (3H, s, 7-CH_3), 7.06 (1H, br s, 6-H), 7.13 (1H, s, 3-H), 7.48 (1H, br s, 8-H) and 11.71 (1H, s, 5-OH); mass spectrum: *m/e* 222/224 (M^+). (Found: C, 59.48; H, 3.23; Cl, 16.04. Calc for $C_{11}H_7ClO_3$: C, 59.35; H, 3.17; Cl, 15.95%).

(b) In a similar experiment (method B), chromatography gave **20a** (33%) and **20b** (9%), m.p. 149–150° (benzene-petroleum ether, b.p. 90–120°); IR ν_{max} (KBr) 1682, 1650, 1595, 1467 and 1260 cm^{-1}; UV λ_{max} (EtOH) 233, 277, 348 and 402 nm (log ϵ 4.15, 3.93, 3.33 and 3.34); NMR ($CDCl_3$) δ 2.52 (3H, s, 7-CH_3), 4.04 (3H, s, 5-OCH_3), 7.12 (1H, s, 3-H), 7.17 (1H, br s, 6-H) and 7.68 (1H, br s, 8-H); mass spectrum: *m/e* 236/238 (M^+).

5-Hydroxy-3-methoxy-7-methylnaphthoquinone (**21a**). Cycloaddition of diene **8** to **13** (method B) after aromatization and separation by chromatography ($CHCl_3$), provided **21a** (25%), m.p. 210–211° (petroleum ether, b.p. 90–120°) (lit.[20] m.p. 209°); IR ν_{max} (KBr) 1650, 1612, 1598, 1370, 1240 and 1222 cm^{-1}; UV λ_{max} (EtOH) 246, 289, 369 and 412 nm (log ϵ 4.68, 4.30, 3.26 and 3.75); NMR ($CDCl_3$) δ 2.43 (3H, br s, 7-Me), 3.90 (3H, s, 3-OCH_3), 6.12 (1H, s, 2-H), 7.05 (1H, m, 6-H), 7.45 (1H, m, 8-H) and 11.77 (1H, s, 5-OH); mass spectrum: *m/e* 218 (M^+). (Found: C, 66.20; H, 4.71. Calc for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62%).

5-Hydroxy-2, 7-dimethoxynaphthoquinone (**22a**). An analogous reaction using **14** and diene **7** (method A), after chromatography (toluene) gave **22a** (20%), m.p. 262.5–263.5° (EtOH) (lit.[21] m.p. 264–266°); IR ν_{max} (KBr) 1684, 1623, 1591, 1383 and 1240 cm^{-1}; UV λ_{max} (EtOH) 262, 304 and 434 nm (log ϵ 3.93, 3.75 and 3.33); NMR (TFA) δ 4.02 (6H, s, 2, 7-OCH_3), 6.43 (1H, s, 3-H), 6.90 (1H, d, J = 2.0 Hz, 6-H) and 7.50 (1H, d, J = 2.0 Hz, 8-H); mass spectrum: *m/e* 234 (M^+).

Methylation of **22a** (CH_3I-Ag_2O) gave **22b** identical to an authentic sample.[15a]

5-Hydroxy-2, 3, 7-trimethoxynaphthoquinone (**23a**). The reaction between **15** and diene **7** (method C) gave **23a** (86%) after chromatography (benzene–CCl_4 1:1), m.p. 109–110° (benzene–petroleum ether, b.p. 30–80°); IR ν_{max} (KBr) 1670, 1630, 1605 and 1590 cm^{-1}; UV λ_{max} (EtOH) 266, 312 and 430 nm (log ϵ 3.66, 3.48 and 3.04); NMR ($CDCl_3$) δ 3.81, 3.99 and 4.03 (3 × 3H, 3s, 2, 3, 7-OCH_3), 6.44 (1H, d, J = 2.5 Hz, 6-H), 7.02 (1H, d, J = 2.5 Hz, 8-H) and 11.97 (1H, s, 5-OH); mass spectrum: *m/e* 264 (M^+). (Found: C, 59.27; H, 4.87. Calc for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58%).

3-Chloro-5-hydroxy-6-methoxynaphthoquinone (**24a**). Compound **24a** was obtained from **11** and diene **9** (method A) after chromatography (benzene–CCl_4 1:1) in 81% yield, m.p. 210–211° (benzene–petroleum ether, b.p. 30–80°); IR ν_{max} (KBr) 1653, 1642, 1590, 1448 and 1262 cm^{-1}; UV λ_{max} (EtOH) 273, 343 and 462 nm (log ϵ 4.10, 2.02 and 3.61); NMR ($CDCl_3$) δ 4.04 (3H, s, 6-OCH_3), 7.16 (1H, d, J = 9.0 Hz, 7-H), 7.21 (1H, s, 2-H), 7.70 (1H, d, J = 9.0 Hz, 8-H) and 12.16 (1H, s, 5-OH); mass spectrum: *m/e* 238/240 (M^+). (Found: C, 55.67; H, 3.08; Cl, 15.09. Calc for $C_{11}H_7ClO_4$: C, 55.37; H, 2.96; Cl, 14.86%).

3-Chloro-5-hydroxy-6-methylnaphthoquinone (**25a**) *and its 5-methyl ether* **25b**.

The condensation of **11** and diene **10** (method C) gave 23% of the desired **25a** after chromatography (CCl_4), m.p. 157–158° (EtOH); IR ν_{max} (KBr) 1650, 1630, 1585 and 1243 cm^{-1}; UV λ_{max} (EtOH) 277 and 436 nm (log ϵ 4.05 and 3.63); NMR ($CDCl_3$) δ 2.38 (3H, s, 6-CH_3), 7.23 (1H, s, 2-H), 7.60 (2H, s, 7, 8-H) and 12.11 (1H, s, 5-OH); mass spectrum: *m/e* 222/224 (M^+). (Found: C, 59.55; H, 3.13; Cl, 16.09. Calc for $C_{11}H_7ClO_3$: C, 59.35; H, 3.17; Cl, 15.93%).

Methylation (MeI-Ag_2O) of the foregoing compound gave the **25b**, m.p. 144–145° after chromatography (benzene–EtOAc 5:1); IR ν_{max} (KBr) 1677, 1662, 1607, 1572, 1290, 1262 and 1245 cm^{-1}; UV λ_{max} (EtOH) 254, 272, 346 and 371 nm (log ϵ 4.11, 4.03, 3.49 and 3.42); NMR (60 MHz; $CDCl_3$) δ 2.43 (3H, s, 6-CH_3), 3.90 (3H, s, 5-OCH_3), 7.18 (1H, s, 2-H) and 7.74 (2H, dd, $\Delta\nu$ = 20.5 Hz, J = 8.0 Hz, 7, 8-H).

2-Chloro-5-hydroxy-6-methoxynaphthoquinone (**26a**). Chromatography (benzene–CCl_4 1:1) of the crude product obtained from **12** and diene **9** (method A) gave **26a** (47%), m.p. 211–212° (benzene–hexane); IR ν_{max} (KBr) 1663, 1630, 1580, 1272 and 1248 cm^{-1}; UV λ_{max} (EtOH) 274, 285 (sh) and 456 nm (log ϵ 3.96, 3.86 and 3.52); NMR ($CDCl_3$) δ 4.04 (3H, s, 6-OCH_3), 7.14 (1H, d, J = 8.0 Hz, 7-H), 7.22 (1H, s, 3-H), 7.82 (1H, d, J = 8.0 Hz, 8-H), and 12.18 (1H, s, 5-OH); mass spectrum: *m/e* 238/240 (M^+). (Found:C, 55.68; H,

3.09; Cl, 14.92. Calc for $C_{11}H_7ClO_4$: C, 55.37; H, 2.96; Cl, 14.86%).

2-Chloro-5-hydroxy-6-methylnaphthoquinone (**27a**) *and its 5-methyl ether* **27b**

(a) An analogous reaction between **12** and diene **10** (method A) gave the required **27a** (32%), after purification by chromatography (benzene), m.p. 159.5–160.5° (petroleum ether, b.p. 90–120°) (lit.[22] m.p. 158–159°), found to be identical to an authentic sample; IR ν_{max} (KBr) 1670, 1630, 1585, 1425 and 1250 cm^{-1}; UV λ_{max} (EtOH) 278 and 438 nm (log ϵ 4.04 and 3.66); NMR ($CDCl_3$) δ 2.39 (3H, br s, 6-CH_3), 7.20 (1H, s, 3-H), 7.43 (1H, br d, J = 8.0 Hz, 7-H), 7.56 (1H, d, J = 8.0 Hz, 8-H) and 12.20 (1H, s, 5-OH); mass spectrum: *m/e* 222/224 (M$^+$).

(b) Methylation of the crude product with MeI and Ag_2O gave **27b**, m.p. 133.5–134.5° (ligroin); IR ν_{max} (KBr) 1669, 1651, 1605, 1569, 1280, 1260 and 1240 cm^{-1}; UV λ_{max} (EtOH) 252, 274, 290 (sh) and 348 nm (log ϵ 3.89, 3.77, 3.61 and 3.31); NMR (60 MHz; $CDCl_3$) δ 2.43 (3H, s, 6-CH_3), 3.88 (3H, s, 5-OCH_3), 7.21 (1H, s, 3-H) and 7.79 (2H, dd, $\Delta\nu$ = 29.5 Hz, J = 8.0 Hz, 7, 8-H).

5-Hydroxy-6-methoxy-2-methylnaphthoquinone (**28a**). Purification of the mixture (CCl_4) obtained from **16** and diene **9** (method B) gave **28a** (13%), m.p. 173.0–173.5° (EtOH) (lit.[23] m.p. 172–173°); IR ν_{max} (KBr) 1665, 1635, 1600 and 1254 cm^{-1}; UV λ_{max} (EtOH) 266 and 444 nm (log ϵ 4.02 and 3.54); NMR ($CDCl_3$) δ 2.18 (3H, d, J = 1.0 Hz, 2-CH_3), 4.00 (3H, s, 6-OCH_3), 6.80 (1H, br s, 3-H), 7.04 (1H, d, J = 8.0 Hz, 7-H), 7.58 (1H, d, J = 8.0 Hz, 8-H) and 12.52 (1H, s, 5-OH); mass spectrum: *m/e* 218 (M$^+$).

Methylation of this compound (MeI-Ag_2O) gave **28b** (77%), m.p. 181–183° (lit.[23] m.p. 184°); IR ν_{max} (KBr) 1655, 1625, 1572 and 1260 cm^{-1}; UV λ_{max} (EtOH) 260 and 392 nm (log ϵ 4.32 and 3.59); NMR (60 MHz; $CDCl_3$) δ 2.15 (3H, d, J = 2.0 Hz, 2-CH_3), 3.92 and 3.98 (2 × 3H, 2s, 5, 6-OCH_3), 6.73 (1H, m, 3-H), 7.20 (1H, d, J = 8.0 Hz, 7-H) and 7.98 (1H, d, J = 8.0 Hz, 8-H).

1-Hydroxy-3-methoxyanthraquinone (**35a**). A reaction involving **29** and **7** (method D) after chromatography (benzene) gave the desired **35a** (99%), m.p. 193–194° (lit.[24] m.p. 193–194°), indistinguishable with an authentic sample; IR ν_{max} (KBr) 1685, 1645, 1605 and 1293 cm^{-1}; UV λ_{max} (EtOH) 240, 243 (sh), 266 (sh), 280 and 408 nm (log ϵ 4.14, 4.12, 4.00, 4.08 and 3.52); NMR ($CDCl_3$) δ 3.78 (3H, s, 3-OCH_3), 6.05 (1H, d, J = 2.5 Hz, 2-H), 7.14 (1H, d, J = 2.5 Hz, 4-H), 7.52 (2H, m, 6, 7-H), 8.00 (2H, m, 5, 8-H) and 12.64 (1H, s, 1-OH); mass spectrum: *m/e* 254 (M$^+$).

1, 8-Dihydroxy-3-methoxyanthraquinone (**36a**). Cycloaddition of diene **7** to **31** (method C) after chromatography (hexane EtOAc acetate 5:1) gave **36a** (53%), m.p. 183–184° (ligroin–benzene 4:1) (lit.[25] m.p. 180°); IR ν_{max} (KBr) 1673, 1627, 1610, 1576, 1278 and 1225 cm^{-1}; UV λ_{max} (EtOH) 245, 265, 284, and 432 nm (log ϵ 4.16, 4.19, 4.18 and 4.04); NMR ($CDCl_3$) δ 3.95 (3H, s, 3-OCH_3), 6.75 (1H, d, J = 2.5 Hz, 2-H), 7.33 (1 H, dd, J = 8.0, 1.5 Hz, 7-H), 7.42 (1H, d, J = 2.5 Hz, 4-H), 7.67 (1H, dd, J = 7.0, 8.0 Hz, 6-H), 7.86 (1H, dd, J = 7.0, 1.5 Hz, 5-H), 12.32 (1H, s, 1-OH) and 12.40 (1H, s, 8-OH); mass spectrum: *m/e* 270 (M$^+$). (Found: C, 66.83; H, 3.90. Calc for $C_{15}H_{10}O_5$: C 66.66; H, 3.73%).

Methylation of this compound (MeI-Ag_2O) afforded **36b**, m.p. 195–196° (lit.[26] m.p. 194.5–195.0°) identical to a previously prepared sample.

1-Hydroxy-3-methylanthraquinone (*Pachybasin*) (**37a**) *and its 1-methyl ether* **37b**. An analogous reaction between **29** and diene **8** (method C) after chromatography (CCl_4–benzene 1:1) gave pachybasin (92%), m.p. 174–175° (MeOH) (lit.[27] m.p. 176–177°); IR ν_{max} (KBr) 1668, 1636, 1590 and 1295 cm^{-1}; UV λ_{max} (EtOH) 246, 254, 259, 282 (sh) and 400 nm (log ϵ 3.95, 3.97, 3.97, 3.66 and 3.38); NMR ($CDCl_3$) δ 2.47 (3H, s, 3-CH_3), 7.14 (1H, br s, 2-H), 7.68 (1H, br s, 4-H), 7.78 (2H, m, 6, 7-H), 8.26–8.40 (2H, m, 5, 8-H) and 12.59 (1H, s, 1-OH); mass spectrum: *m/e* 238 (M$^+$). Continued elution with the same solvent gave **37b** (3%), m.p. 187–188° (lit.[27] m.p. 185–187°), indistinguishable with an authentic sample; IR ν_{max} (KBr) 1666, 1598, 1350 and 1285 cm^{-1}; UV λ_{max} (EtOH) 256, 326 and 388 nm (log ϵ 4.42, 3.44 and 3.70); NMR ($CDCl_3$) δ 2.47 (3H, br s, 3-CH_3), 4.03 (3H, s, 1-OCH_3), 7.12 (1H, br s, 2-H), 7.57–7.89 (3H, m, 4, 6, 7-H) and 8.06–8.37 (2H, m, 5, 8-H); mass spectrum: *m/e* 252 (M$^+$).

1, 5-Dihydroxy-3-methylanthraquinone (*Ziganein*) (**38a**). Condensation of **30** and diene **8** (method A) after chromatography (benzene–CCl_4 1:1) gave **38a** (55%), m.p. 226–227° (MeOH) (lit.[28] m.p. 227–228°); the IR spectrum of which was superposable on that of the authentic material; IR ν_{max} (KBr) 1622, 1582, 1382, 1335 and 1273 cm^{-1}; UV λ_{max} (EtOH) 254, 280, 290 and 430 nm (log ϵ 4.31, 3.99, 4.01 and 4.01); NMR ($CDCl_3$) δ 2.45 (3H, s, 3-CH_3), 7.08 (1H, br s, 2-H), 7.22–7.72 (3H, m, 4, 6, 7-H), 7.79 (1H, dd, J = 7.5, 1.5 Hz, 8-H), 12.56 and 12.62 (2H, 2s, 1, 5-OH); mass spectrum: *m/e* 254 (M$^+$).

1, 8-Dihydroxy-3-methylanthraquinone (*Chrysophanol*) (**39a**) *and its 1-methyl ether* **39b**. Reaction between **31** and diene **8** (method D) gave chrysophanol (63%), m.p. 194–195° (petroleum ether, b.p. 90–120°) (lit.[29] m.p. 195–196°); IR ν_{max} (KBr) 1673, 1625, 1605 and 1270 cm^{-1}; UV λ_{max} (EtOH) 256, 277, 287, and 430 nm (log ϵ 4.02, 3.72, 3.74 and 3.76); NMR ($CDCl_3$) δ 2.48 (3H, s, 3-CH_3), 7.06 (1H, br s, 2-H), 7.29 (1H, dd, J = 7.5, 1.5 Hz, 7-H), 7.56–7.78 (2H, m, 4, 6-H), 7.83 (1H, dd, J = 8.0, 1.5 Hz, 5-H), and 12.00 and 12.11 (2H, 2s, 1, 8-OH); mass spectrum: *m/e* 254 (M$^+$).

A second zone was separated by chromatography (benzene–EtOAc 50:1) and gave methyl 3-methyl-4-[3-chloro-5-hydroxynaphthoquinonyl-2]-2-butenoate (< 1%), m.p. 132–133° (petroleum ether, b.p. 90–120°) (method B gave a 14% yield of this compound along with 22% of chrysophanol); IR ν_{max} (KBr) 1717, 1661, 1632, 1603 and 1213 cm^{-1}; NMR ($CDCl_3$) δ 2.28 (3H, br s, 3-CH_3), 3.67 (5H, s, 1-OCH_3 and 4-H), 5.61 (1H, m, 2-H), 7.33 (1H, m, 6'-H), 7.70 (2H, m, 7', 8'-H) and 11.73 (1H, s, 5'-OH); mass spectrum: *m/e* 320/322 (M$^+$).

A slower moving band consisted of **39b** (4%), m.p. 199–200° (petroleum ether, b.p. 90–120°) (lit.[30] m.p. 198–200°); IR ν_{max} (KBr) 1670, 1626, 1602 and 1256 cm^{-1}; UV λ_{max} (EtOH) 258, 275 (sh), 283 and 414 nm (log ϵ 3.96, 3.75, 3.70 and 3.64); NMR ($CDCl_3$) δ 2.52 (3H, br s, 3-CH_3), 4.09 (3H, s, 1-OCH_3), 7.18 (1H, br s, 2-H), 7.32 (1H, dd, J = 8.0, 2.0 Hz, 7-H), 7.64 (1H, ~t, J = 8.0, 8.0 Hz, 6-H), 7.81 (1H, dd, J = 8.0, 2.0 Hz, 5-H), 7.82 (1H, br s, 4-H) and 13.09 (1H, s, 8-OH).

1-Hydroxy-8-methoxy-3-methylanthraquinone (*Chrysophanol 8-methyl ether*) (**39c**) *and chrysophanol dimethyl ether* (**39d**). A similar reaction between **32** and diene **8** (method A) gave **39c** (50%), m.p. 192–193° (benzene–ligroin) (lit.[29] m.p. 195°); IR ν_{max} (KBr) 1675, 1635, 1580, 1445, 1275 and 1245 cm^{-1}; UV λ_{max} (EtOH) 262 and 400 nm (log ϵ 4.06 and 3.63); NMR ($CDCl_3$) δ 2.47 (3H, s, 3-CH_3), 4.12 (3H, s, 8-OCH_3), 7.14 (1H, br s, 2-H), 7.40 (1H, dd, J = 8.5, 1.5 Hz, 7-H), 7.64 (1H, br s, 4-H), 7.78 (1H, dd, J = 8.5, 8.0 Hz, 6-H), 8.02 (1H, dd, J = 8.0, 1.5 Hz, 5-H) and 12.98 (1H, s, 1-OH); mass spectrum: *m/e* 268 (M$^+$).

A second band afforded **39d** (44%), m.p. 196.0–196.5° (benzene–petroleum ether, b.p. 30–80°) (lit.[31] m.p. 190°); IR ν_{max} (KBr) 1670, 1601, 1575, 1280 and 1230 cm^{-1}; UV λ_{max} (EtOH) 257 and 394 nm (log ϵ 4.24 and 3.75); NMR ($CDCl_3$) δ 2.50 (3H, br s, 3-CH_3), 4.04 and 4.05 (2 × 3H, 2s, 1, 8-OCH_3), 7.14 (1H, br s, 2-H), 7.33 (1H, dd, J = 8.0, 2.0 Hz, 7-H), 7.67 (1H, dd, J = 8.0, 7.5 Hz, 6-H), 7.71 (1H, br s, 4-H) and 7.88 (1H, dd, J = 7.5, 2.0 Hz, 5-H); mass spectrum: *m/e* 282 (M$^+$).

1, 4, 8-Trihydroxy-6-methylanthraquinone (*Helminthosporin*) (**40a**) *and its 8-methyl ether* **40b**. Condensation of **33** with diene **8** (method A) gave **40a** (85%), m.p. 228–229° (pyridine) (lit.[26] m.p. 226–227°), identical with an authentic sample; IR ν_{max} (KBr) 1597, 1570, 1450 and 1235 cm^{-1}; UV

λ_{max} (EtOH) 254, 288, 294 (sh), 478, 488, 508 and 522 nm (log ϵ 3.84, 3.50, 3.49, 3.66, 3.69, 3.57 and 3.49); NMR ($CDCl_3$) δ 2.47 (3H, s, 6-CH_3), 7.08 (1H, br s, 7-H), 7.22 (2H, s, 2, 3-H), 7.66 (1H, br s, 5-H) and 12.09, 12.28 and 12.96 (3 × 1H, 3s, 1, 4, 8-OH); mass spectrum: *m/e* 270 (M^+).

CCl_4 eluted a slower moving zone consisting of **40b** (10%), m.p. 275–276° (benzene–petroleum ether, b.p. 60–80°); IR ν_{max} (KBr) 1622, 1596, 1450, 1309, 1210 and 1200 cm^{-1}; UV λ_{max} (EtOH) 255, 476, 488 and 524 nm (log ϵ 4.02, 3.84, 3.81 and 3.49); NMR ($CDCl_3$) 2.54 (3H, s, 6-CH_3), 4.09 (3H, s, 8-OCH_3), 7.19 (1H, br s, 7-H), 7.29 (2H, s, 2, 3-H), 7.88 (1H, br s, 5-H), 12.89 and 13.33 (2 × 1H, 2s, 1, 4-OH); mass spectrum: *m/e* 284 (M^+).

1, 5-*Dihydroxy*-2-*methylanthraquinone* (*Isoziganein*) (**41a**) *and its* 1-*methyl ether* **41b**. An analogous reaction with **30** and diene **10** (method A) after purification by chromatography (benzene) gave **41a** (33%), m.p. 189–190° (MeOH) (lit.[32] m.p. 194°); IR ν_{max}(KBr) 1625, 1608, 1568, 1451, 1315 and 1267 cm^{-1}; UV λ_{max} (EtOH) 255, 279, 289, 426 (sh) and 434 nm (log ϵ 4.32, 3.93, 3.96, 3.98 and 3.99); NMR ($CDCl_3$) δ 2.41 (3H, s, 2-CH_3), 7.33 (1H, dd, J = 8.0, 1.5 Hz, 6-H), 7.58 (1H, d, J = 7.5 Hz, 3-H), 7.71 (1H, dd, J = 7.0, 8.0 Hz, 7-H), 7.74 (1H, d, J = 7.5 Hz, 4-H), 7.87 (1H, dd, J = 7.0, 1.5 Hz, 8-H), 12.82 (1H, s, 1-OH) and 13.02 (1H, s, 5-OH); mass spectrum: *m/e* 254 (M^+).

A second zone was separated by chromatography (benzene-CCl_4 1:1) and provided **41b** (21%), m.p. 160–161°; IR ν_{max} (KBr) 1672, 1635, 1578, 1450 and 1257 cm^{-1}; UV λ_{max} (EtOH) 255, 280 and 402 nm (log ϵ 4.25, 3.83 and 3.68); NMR (60 MHz; $CDCl_3$) δ 2.43 (3H, s, 2-CH_3), 3.93 (3H, s, 1-OCH_3), 7.25 (1H, dd, J = 2.5, 7.0 Hz, 6-H), 7.53–7.90 (3H, m, 3, 7, 8-H), 8.08 (1H, d, J = 8.0 Hz, 4-H) and 12.60 (1H, s, 5-OH).

1, 8-*Dihydroxy*-2-*methylanthraquinone* (*Isochrysophanol*) (**42a**) *and its* 1-*methyl ether* **42b**. A reaction between **31** and diene **10** (method A) gave **42a** (36%), m.p. 174.0–174.5° (benzene-petroleum ether, b.p. 30–80°) (lit.[33] m.p. 174–175°), indistinguishable with an authentic sample; IR ν_{max} (KBr) 1672, 1622, 1595, 1465 and 1428 cm^{-1}; UV λ_{max} (EtOH) 256, 287 and 432 nm (log ϵ 4.35, 3.99 and 4.05); NMR ($CDCl_3$) δ 2.37 (3H, s, 2-CH_3), 7.28 (1H, dd, J = 8.0, 2.0 Hz, 7-H), 7.52 (1H, br d, J = 7.5 Hz, 3-H), 7.67 (1H, dd, J = 7.0, 8.0 Hz, 6-H), 7.73 (1H, d, J = 7.5 Hz, 4-H), 7.82 (1H, dd, J = 7.0, 2.0 Hz, 5-H), 12.08 (1H, s, 1-OH) and 12.37 (1H, s, 8-OH); mass spectrum: *m/e* 254 (M^+).

Elution with benzene gave **42b** (12%), m.p. 154–156° (petroleum ether, b.p. 80–110°); IR ν_{max} (KBr) 1670, 1634, 1472 and 1251 cm^{-1}; UV λ_{max} (EtOH) 257, 282 and 400 nm (log ϵ 4.31, 3.76 and 3.88); NMR ($CDCl_3$) δ 2.45 (3H, s, 2-CH_3), 3.96 (3H, s, 1-OCH_3), 7.31 (1H, dd, J = 8.0, 1.7 Hz, 7-H), 7.66 (1H, d, J = 7.7 Hz, 3-H), 7.66 (1H, dd, J = 7.0, 8.0 Hz, 6-H), 7.82 (1H, dd, J = 7.0, 1.7 Hz, 5-H), 8.08 (1H, d, J = 7.7 Hz, 4-H) and 12.96 (1H, s, 8-OH); mass spectrum: *m/e* 268 (M^+).

1-*Hydroxy*-2-*methoxyanthraquinone* (*Alizarin* 2-*methyl ether*) (**43a**) *and alizarin dimethyl ether* **43b**. Condensation of **29** and diene **9** (method A) followed by chromatography (benzene then benzene–EtOAc 5:1) gave **43a** (75%), m.p. 232–233° (benzene–petroleum ether, b.p. 90–120°) (lit.[34] m.p. 231°); IR ν_{max} (KBr) 1665, 1637, 1590, 1457 and 1368 cm^{-1}; UV λ_{max} (EtOH) 247, 277, 376 and 424 nm (log ϵ 4.37, 4.02, 3.36 and 3.69); NMR ($CDCl_3$) δ 4.07 (3H, s, 2-OCH_3), 7.22 (1H, d, J = 9.0 Hz, 3-H), 7.77–7.94 (3H, m, 4,6,7-H), 8.24–8.41 (2H, m, 5, 8-H) and 12.91 (1H, s, 1-OH); mass spectrum: *m/e* 254 (M^+).

A second zone consisted of **43b** (3%), m.p. 200–203° (benzene–petroleum ether, b.p. 90–120°) (lit.[35] m.p. 208°); IR ν_{max} (KBr) 1669, 1570, 1333 and 1267 cm^{-1}; UV λ_{max} (EtOH) 249, 263 and 385 nm (log ϵ 4.20, 4.14 and 3.47); mass spectrum: *m/e* 268 (M^+).

1,5-*Dihydroxy*-2-*methoxy*-6-*methylanthraquinone* (*Morindone* 6-*methyl ether*) (**44a**) *and its* 1-*methyl ether* **44b**. Purification by chromatography (benzene) of the mixture obtained from **27a** and the diene **9** (method A) gave **44a** (63%), m.p. 252–253° (benzene–petroleum ether, b.p. 30–80°) (lit.[36] m.p. 248°); IR ν_{max} (KBr) 1620, 1580, 1375 and 1250 cm^{-1}; UV λ_{max} (EtOH) 260, 290, 299 and 444 nm (log ϵ 4.38, 3.93, 3.97 and 3.99); NMR (60 MHz; TFA) δ 2.38 (3H, s, 6-CH_3) and 4.08 (3H, s, 2-OCH_3); mass spectrum: *m/e* 284 (M^+).

Continuing to elute with benzene-EtOAc 10:1 provides **44b** (10%), m.p. 238.5–239.5° (petroleum ether, b.p. 65–110°); IR ν_{max} (KBr) 1670, 1625, 1570, 1485 and 1264 cm^{-1}; UV λ_{max} (EtOH) 267, 292, and 410 nm (log ϵ 4.33, 4.07 and 3.94); NMR ($CDCl_3$) δ 2.39 (3H, s, 6-CH_3), 4.02 and 4.04 (2 × 3H, 2s, 1, 2-OCH_3) and 13.03 (1H, s, 5-OH); mass spectrum: *m/e* 298 (M^+).

Methylation (MeI-Ag_2O) of the principal product **44a** gave the **44c** (quant.), m.p. 235–236° (acetone) (lit.[36] m.p. 237–238°); IR ν_{max} (KBr) 1668, 1570, 1330 and 1268 cm^{-1}; UV λ_{max} (EtOH) 255, 267 (sh), 287 (sh) and 362 nm (log ϵ 4.32, 4.29, 4.10 and 3.76); NMR ($CDCl_3$) δ 2.44 (3H, s, 6-CH_3), 3.96 (3H, s, 2-OCH_3), 4.03 (6H, s, 1, 5-OCH_3), 7.27 (1H, d, J = 8.5 Hz, 3-H), 7.57 (1H, d, J = 7.5 Hz, 7-H), 7.99 (1H, d, J = 7.5 Hz, 8-H) and 8.11 (1H, d, J = 8.5 Hz, 4-H); mass spectrum: *m/e* 312 (M^+).

1-*Hydroxy*-2-*methylanthraquinone* (**45a**) *and its methyl ether* **45b**. The crude product from a reaction between **29** and diene **10** (method A) was separated by chromatography (benzene–CCl_4 1:1) giving **45a** (56%), m.p. 182.0–182.5° (benzene–petroleum ether, b.p. 90–120°) (lit.[37] m.p. 180–182°); IR ν_{max} (KBr) 1672, 1635, 1592, 1360 and 1295 cm^{-1}; UV λ_{max} (EtOH) 253 and 408 nm (log ϵ 4.17 and 3.52); mass spectrum: *m/e* 238 (M^+).

Elution with benzene-EtOAc 10:1 gave **45b** (21%), m.p. 164–165° (petroleum ether, b.p. 65–110°) (lit.[36] m.p. 166.5–167.0°); IR ν_{max} (KBr) 1670, 1569, 1327, 1318, 1273, 1261 and 705 cm^{-1}; UV λ_{max} (EtOH) 255 and 352 nm (log ϵ 4.41 and 3.52); mass spectrum: *m/e* 252 (M^+).

5-*Hydroxy*-1, 2, 3-*trimethoxy*-6-*methylanthraquinone* (*Copareolatin* 5, 6, 7-*trimethyl ether*) (**46a**) *and the tetramethyl ether* **46b**. Anthraquinone **46a** was obtained (41%) from **34**[1] and diene **10** (method A) after chromatography (benzene-EtOAc 50:1), m.p. 178.0–178.5° (benzene–petroleum ether, b.p. 90–120°); IR ν_{max} (KBr) 1660, 1640, 1570, 1359 and 1132 cm^{-1}; UV λ_{max} (EtOH) 276 and 408 nm (log ϵ 4.42 and 3.80); NMR ($CDCl_3$) δ 2.37 (3H, br s, 6-CH_3), 4.02 and 4.04 (2 × 3H, 2s, 2, 3-OCH_3), 4.16 (3H, s, 1-OCH_3), 7.53 (1H, br d, J = 8.0 Hz, 7-H), 7.73 (1H, s, 4-H), 7.73 (1H, d, J = 8.0 Hz, 8-H) and 12.82 (1H, s, 5-OH); mass spectrum: *m/e* 328 (M^+).

A second zone (benzene–EtOAc 10:1) consisted of the permethylated deriv **46b** (14%), m.p. 182.5–183.0° (benzene–petroleum ether, b.p. 65–110°) (lit.[1] m.p. 181–182°) identical to a sample obtained earlier; IR ν_{max} (KBr) 1668, 1570, 1335, 1320 and 1288 cm^{-1}; UV λ_{max} (EtOH) 276 and 360 nm (log ϵ 4.42 and 3.71); NMR ($CDCl_3$) δ 2.44 (3H, s, 6-CH_3), 3.96, 4.03, 4.04 and 4.08 (4 × 3H, 4s, 1, 2, 3, 5-OCH_3), 7.61 (1H, d, J = 7.5 Hz, 7-H), 7.71 (1H, s, 4-H) and 8.04 (1H, d, J = 7.5 Hz, 8-H); mass spectrum: *m/e* 342 (M^+).

1, 8-*Dihydroxy*-3-*methoxy*-6-*methylanthraquinone* (*Physcion*) (**47a**)

(a) Physcion **47a** was obtained (68%) from **17a** and diene **8** (method C) eluting with benzene-$CHCl_3$ 1:1, m.p. 206.0–206.5° (benzene–petroleum ether, b.p. 90–120°) (lit.[38] m.p. 206–207°); IR ν_{max} (KBr) 1677, 1618, 1598, 1560, 1480 and 1155 cm^{-1}; UV λ_{max} (EtOH) 253, 265 and 434 nm (log ϵ 3.93, 3.94 and 3.77); RMN ($CDCl_3$) δ 2.44 (3H, s, 6-CH_3), 3.92 (3H, s, 3-OCH_3), 6.62 (1H, d, J = 2.0 Hz, 2-H), 7.01 (1H, br s, 7-H), 7.29 (1H, d, J = 2.0 Hz, 4-H), 7.56 (1H, br s, 5-H), 12.00 and 12.20 (2 × 1H, 2s, 1, 8-OH); mass spectrum: *m/e* 284 (M^+).

A second zone was separated (benzene–EtOAc 50:1) and gave methyl 3-methyl-4-[3-chloro-5-hydroxy-7-methoxynaphthoquinonyl-2]-2-butenoate (10%), m.p. 130–131° (benzene–ligroin); IR ν_{max} (KBr) 1720, 1659, 1622, 1600, 1299, 1201 and 1142 cm^{-1}; UV λ_{max} (EtOH) 268, 297 and 430 nm (log ϵ 4.08, 3.98 and 3.59); NMR ($CDCl_3$) δ 2.28

(3H, br s, 3-Me), 3.66 (2H, br s, 4-H), 3.68 (3H, s, 1-OCH_3), 3.94 (3H, s, 7'-OCH_3), 5.63 (1H, br s, 2-H), 6.71 (1H, d, J = 2.0 Hz, 6'-H), 7.24 (1H, d, J = 2.0 Hz, 8'-H) and 11.98 (1H, s, 5'-OH); mass spectrum: *m/e* 350/352 (M^+). (Found: C, 58.47; H, 4.34; Cl, 10.09. Calc for $C_{17}H_{15}ClO_6$: C, 58.21; H, 4.31; Cl, 10.10%). A slower moving fraction consisted of **47b** (8%).

(b) Naphthoquinone **18a** and diene **7** (method A) gave the same **47a** (72%) after chromatography (CCl_4–benzene 1:1) and recrystallization ($CHCl_3$–EtOH).

A slower moving band gave the **47c** (9%).

1-*Hydroxy*-3, 8-*dimethoxy*-6-*methylanthraquinone* ("*Emodin* 1, 6-*dimethyl ether*") (**47c**). Cycloaddition of diene **7** to **18b** (method A) after chromatography (benzene EtOAc 1:1) gave **47c** (83%), m.p. 194–196° (EtOH–water) (lit.[39] m.p. 193–195°); IR ν_{max} (KBr) 1690, 1631, 1598, 1335, 1264, 1243 and 1158 cm^{-1}; UV λ_{max} (EtOH) 252, 268, 283 and 424 nm (log ϵ 4.22, 4.24, 4.29 and 3.97); NMR ($CDCl_3$) δ 2.50 (3H, s, 6-CH_3), 3.93 and 4.06 (2 × 3H, 2s, 3, 8-OCH_3), 6.69 (1H, d, J = 2.5 Hz, 2-H), 7.14 (1H, br s, 7-H), 7.29 (1H, d, J = 2.5 Hz, 4-H), 7.74 (1H, br s, 5-H) and 13.33 (1H, s, 1-OH); mass spectrum: *m/e* 298 (M^+).

A slower moving product was identified as **47d** (4%), m.p. 227–228° (lit.[40] m.p. 227–228°); IR ν_{max} (KBr) 1661, 1600, 1455 and 1318 cm^{-1}; UV λ_{max} (EtOH) 278 and 402 nm (log ϵ 4.27 and 3.73); mass spectrum: *m/e* 312 (M^+).

8-*Hydroxy*-1, 3-*dimethoxy*-6-*methylanthraquinone* ("*Emodin* 6, 8-*dimethyl ether*") (**47b**). A similar reaction between **17b** and diene **8** (method A) gave **47b** (79%) after chromatography (benzene–EtOAc 5:1), m.p. 211° (benzene-petroleum ether, b.p. 30–80°) (lit.[26] m.p. 211°); IR ν_{max} (KBr) 1670, 1630, 1593, 1320 and 1263 cm^{-1}; UV λ_{max} (EtOH) 271, 280 and 422 nm (log ϵ 4.20, 4.21 and 3.87); mass spectrum: *m/e* 298 (M^+).

A second zone (2.6%) was shown to be the abnormal product **48** while a third band consisted of **47d** (11%).

5-*Hydroxy*-1, 3-*dimethoxy*-7-*methylanthraquinone* (**48**). Reaction of **19b** and diene **8** (method A) gave **48** (93%) after chromatography (benzene EtOAc 5:1), m.p. 229–230° (benzene-petroleum ether, b.p. 30–80°); IR ν_{max} (KBr) 1657, 1639, 1613, 1587, 1362 and 1295 cm^{-1}; UV λ_{max} (EtOH) 251, 277, 298 (sh) and 404 nm (log ϵ 4.20, 4.39, 4.16 and 4.06); NMR ($CDCl_3$) δ 2.48 (3H, s, 7-CH_3), 4.03 and 4.05 (2 × 3H, 2s, 1, 3-OCH_3), 6.84 (1H, d, J = 2.5 Hz, 2-H), 7.08 (1H, br s, 6-H), 7.52 (1H, d, J = 2.5 Hz, 4-H), 7.65 (1H, br s, 8-H) and 12.42 (1H, s, 5-OH); mass spectrum: *m/e* 298 (M^+).

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