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Alkoxycarbonylation of Quinones. A Route to Naphthacene Quinones. Reversibility in Homolytic Substitution

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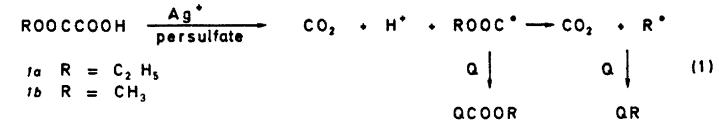
Quinones are alkoxycarbonylated in satisfactory yields by mono esters of oxalic acid and the $Ag^{+}/S_2O_8^{2-}$ couple. Cyclization of the benzyl derivatives gives a new entrance to naphthacene quinones. Product studies present a clearcut example of radical exchange, the mechanism of which is discussed. ^{13}C NMR and ESR data were used for structural determinations of juglone derivatives.

The naphthacene quinones and their hydrogenated derivatives are of interest as a group of compounds housing antibiotics and dyes. Our earlier work showed that quinones can readily be alkylated in satisfactory yields.[1–3] The present work extends this reaction to alkoxycarbonylation, intended to serve as part of a new route into the tetracyclic naphthacene quinone system. By proper substitution it should be possible to synthesize naturally occurring anthracyclinones.

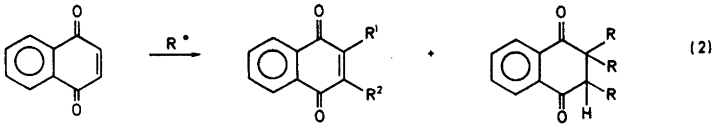
Monoesters of oxalic acid have been used earlier for radical alkoxycarbonylation of N-heterocycles.[4] Quinones efficiently trap the radicals *1a* and *1b* with the formation of esters. Naphthoquinone gives very little of the monoalkoxycarbonylated product, *2b*, which apparently is extremely reactive towards radicals and forms *2a* with *1a* even in excess of naphthoquinone. *2a* gives on further reaction with *1a* small amounts of *3* as was shown by MS. 2-Methylnaphthoquinone reacts similarly, eqns. (1) – (3). Chromatography of the reaction products revealed in addition to *4b* and *4d* (contaminated by some *5a* and *5b*) also small amounts of *4a* and *4c* showing that *1a* and *1b* partly fragment into CO_2 and R$^{\cdot}$ before being trapped by the quinone, Q, eqn. (1). Benzoquinone and toluquinone gave no products which could be isolated under the applied reaction conditions.

Having secured a simple route to alkoxycarbonylated naphthoquinones we set out to test our projected synthesis of naphthacene quinone, eqn. (4). The benzylation and the following ethoxycarbonylation to *6a* worked as anticipated. At this stage of the synthesis, we were struck by the presence of some unexpected minor reaction products. Besides the considerable amounts of ethylated compound *8* and small amounts of the diethoxycarbonylated compound *9*, we found that the mass spectrum of one of the chromatographic fractions contained a peak corresponding to M^{+} of *2e*. It was ascertained that *2e* did not originate from the benzylation step and *2e* was then isolated from one of the faster running fractions, eqn. (5). This finding is only compatible with radical exchange and reversibility of homolytic substitution. Radical 1,2-shift seems also to be of secondary importance. Because of steric hindrance at C_3, *1a* attacks *2d* at C^2 reluctantly; benzyl is expelled and attacks another molecule. The trapping time and consequently the fragmentation of *1a* increases which explains the formation of larger amounts of *8*. The exchange is facilitated by the relative stability of the benzyl radical. The reactions were substantiated by the study of the action of ethyl radicals on *2d*. *2e*, *2g*, and *8* were isolated approximately in the proportion 1:1:10. The mechanism of the homolytic substitution is summarized in eqn. (6) and is characterized by (a) radical exchange and reversibility and (b) an energetically unfavourable 1,2 shift. Ipso-attack and reversibility in



1a R = C_2H_5
1b R = CH_3

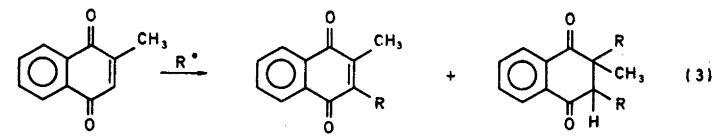
(1)



(2)

3 R = $COOC_2H_5$

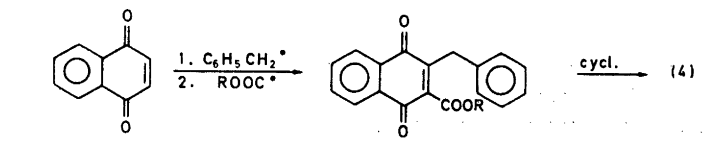
2a $R^1 = R^2 = COOC_2H_5$
2b $R^1 = COOC_2H_5$, $R^2 = H$
2c $R^1 = R^2 = COOCH_3$
2d $R^1 = CH_2C_6H_5$, $R^2 = H$
2e $R^1 = R^2 = CH_2C_6H_5$
2f $R^1 = CH_2C_6H_3\text{-}3,4(OCH_3)_2$, $R^2 = H$
2g $R^1 = R^2 = C_2H_5$



(3)

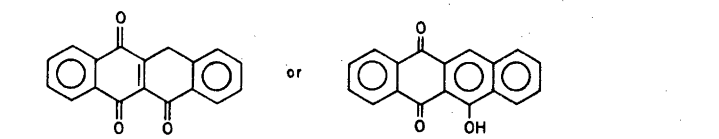
4a R = C_2H_5
4b R = $COOC_2H_5$
4c R = CH_3
4d R = $COOCH_3$

5a R = $COOC_2H_5$
5b R = $COOCH_3$



(4)

6a R = C_2H_5
6b R = CH_3



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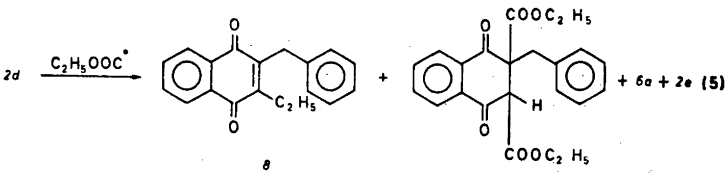

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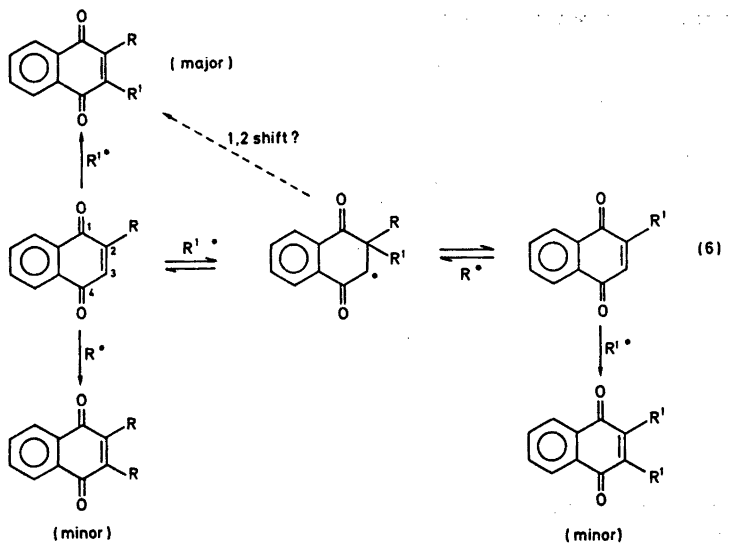
(5)



homolytic aromatic substitutions have now been observed on several occasions.[5–9]

Since the juglone moiety is a common structural element of many polycyclic quinoid natural products, the isomer distribution of homolytic alkylation of juglone *10a* was investigated. Benzylation was chosen as a model reaction and the structural determination was carried out along two lines. The $J^{13}_{C-^1H}$ of a series of naphtho- and anthraquinones were recently determined.[10a] The $^{13}C-^1H$ coupling constants of the easily recognizable carbonyl carbons seemed to be useful for determining positions of substituents but there are apparently also small ^4J couplings of about 1 Hz which broaden the lines and complicate the spectra.

Assuming a value of 4 Hz for $^3J_{C^1CH_3}$ or $^3J_{C^4CH_3}$ approximate linewidths and multiplicities of the C^1 and C^4 peaks in the ^{13}C NMR spectra of *10c* and *10f* can be calculated and compared with the experimental data. However, the assignment can more easily be made from the observation that the hydrogen bonded carbonyl C^4 in juglone derivatives is shifted downfield by *ca.* 6 ppm in comparison with C^5 methoxylated, acetylated, alkylated, or unsubstituted naphthoquinones. In *10c* C^1 (high field CO) appears as a broad doublet and in *10f* C^4 (low field CO) appears as a broad doublet (Table 1). Halogen substitution (Cl, Br) in the quinoid ring shifts the vicinal carbonyl upfield with *ca.* 6 ppm.

The ESR spectra of the anion radicals of the isomeric *10c* and *10f* were recorded and compared with the data from 2-methyljuglone (plumbagin) and other relevant quinones in order to investigate any significant trend or change in spin distributions as a result of the

Table 1. ^{13}C NMR data of naphthoquinones.

Compound	Shift, δ		Coupling constants or Linewidths () Hz	
	C^1	C^4	C^1	C^4
10b	182.0	183.4	br. s. (6.5) [a]	br. d, 8.4 [b]
2,3,6-*Tribromojuglone*	176.9	182.2	br. d, 4.7 [c]	br. s. (3.5)
10c	184.4	190.7	br. d, 11 [d]	br. s. (3)
10f	184.8	190.8	br. s (7)	br. d, 9 [b]

[a] Approx. heptet, J 1 Hz. [b] $J^{13}_{C^4H^8}$ Hz. [c] $J^{13}_{C^1H^8}$ Hz. [d] $J^{13}_{C^1CH_3}$ *ca.* 3.5 Hz, $J^{13}_{C^1H^8}$ 3.5–4 Hz, $J^{13}_{C^1H^{6,7}}$ *ca.* 1.5 Hz, $J^{13}_{C^1H^5}$ 11 Hz.

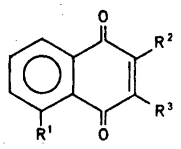
Table 2. Coupling constants of semiquinone radicals.

Compound	a_H gauss, position						
	2	3	5	6	7	8	Substituent
Benzoquinone	2.36	2.36	2.36	2.36			
Toluquinone		1.72	2.54	2.36			2.00
Benzylbenzoquinone		1.88	2.43	2.40			1.57
Naphthoquinone	3.11	3.11	0.55	0.63	0.63	0.55	
2-Methylnaphthoquinone		2.34					3.01
Juglone	3.30	3.05		1.27	0.68	1.27	0.30(OH)
2-Methyljuglone		2.33		1.34 [a]	0.68	1.23 [a]	3.05(CH_3)
							0.28(OH)
2-Benzyljuglone (*10c*)		2.48		1.27 [a]	0.73	1.23 [a]	2.63(CH_2)
							0.30(OH)
3-Benzyljuglone (*10f*)	2.80			1.28	0.75	1.28	2.80(CH_2)
							0.35(OH)

[a] Can be reversed.

substitution pattern that could be used for structural determination. The ESR data support the assigned structure of *10c* and *10f*, especially with reference to the observation that the coupling constant of the vicinal aromatic proton in the semiquinone ring decreases by *ca.* 0.5–0.7 gauss [10b] on alkyl substitution, but the differences of a_H are sometimes on the limit to allow definite conclusions to be drawn about substitution patterns (Table 2).

Benzylation of 3-bromojuglone, debromination with zinc in acetic acid, and reoxidation gave unambiguously the 2-derivative *10c* together with the ketone *11* (major) which unexpectedly is stable to chromic acid in acetic acid (2 h) and does not aromatize spontaneously. *11* could be reoxidized to *10c* by aeration for a short time in alkaline solution. Similar observations have been reported on several occasions.[11–13] Benzylation of juglone gave an inseparable mixture of 2- and 3-benzyljuglones but juglone acetate gave one major product *10d*. The hydrolysis product *10f* proved to be different from *10c*.



10a $R^1 = OH$, R^2, $R^3 = H$

10b $R^1 = OH$, $R^2 = H$, $R^3 = Br$

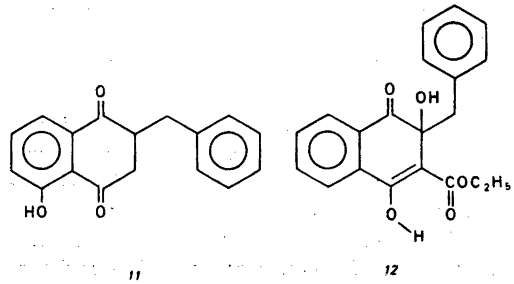
10c $R^1 = OH$, $R^2 = CH_2C_6H_5$, $R^3 = H$

10d $R^1 = OAc$, $R^2 = H$, $R^3 = CH_2C_6H_5$

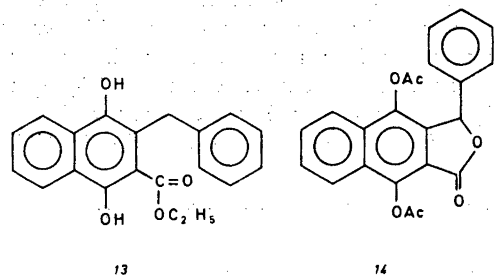
10e $R^1 = OH$, $R^2 = CH_2C_6H_5$, $R^3 = Br$

10f $R^1 = OH$, $R^2 = H$, $R^3 = CH_2C_6H_5$

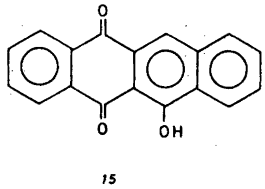
10g $R^1 = OH$, $R^2 = COOCH_3$, $R^3 = Br$



11 *12*



13 *14*



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Treatment of *6a* with base in order to hydrolyze the ester before an attempted cyclization to the tetracyclic system gave the addition product *12* which was resistant to 4 N potassium hydroxide for 24 h. *13*, obtained by zinc reduction of *6a*, was also resistant refluxing 4 N aqueous potassium for 1 h, but some *6a* was formed by aerial oxidation. The acid catalyzed reaction of *6a* with acetic anhydride gave the lactone *14* as one of the products. An attempt to cyclize *6a* in refluxing phosphorus oxychloride or trifluoracetic anhydride gave the starting material back but the naphthacene quinone *15* was finally obtained by treatment of *6a* with polyphosphoric acid (PPA) at 100 °C for 4 h.

EXPERIMENTAL

Diethoxycarbonylation of 1,4-naphthoquinone. To the vigorously stirred solution of 1,4-naphthoquinone (1.58 g, 0.01 mol), potassium salt of monoethyl oxalate (4.68 g, 0.03 mol), silver nitrate (1 g) in acetonitrile (30 ml), and water (30 ml) at 60 – 65 °C was added ammonium peroxydisulfate (6.84 g, 0.03 mol) in water (15 ml) during 10 min. After 1 h the mixture was cooled to room temperature and water (100 ml) was added. Extraction with methylene chloride, washing twice with water (20 ml), drying over Na_2SO_4, and evaporation of the solvent gave an oily liquid (2.05 g) which was purified by chromatography on silica gel (light petroleum/ether, 3:1). The yield of *2a* was 51 %, red oil (lit.[14] m.p. 53.7 – 54.7 °C). According to the ^{1}H NMR and MS *2a* was contaminated with minor amounts of *3*. When 0.015 mol of *1a* was used, the amount of unreacted naphthoquinone increased; *2a* was still the main product but only small amounts of *2b* could be detected. ^{1}H NMR ($CDCl_3$): δ 1.39 (6 H, t, J 6.2 Hz), 4.43 (4 H, q, J 6.2 Hz), 7.7 – 8.2 (4 H, m). A quartet originating from *3* was visible at δ 4.24 (J 7 Hz).

Dimethoxycarbonylation of 1,4-naphthoquinone. To the vigorously stirred solution of 1,4-naphthoquinone (1.58 g, 0.01 mol), potassium salt of monomethyl oxalate (2.84 g, 0.02 mol), silver nitrate (1 g) in acetonitrile (30 ml), and water (30 ml) at 60 – 65 °C was added a solution of ammonium peroxydisulfate (4.56 g, 0.02 mol) in water (10 ml) during 10 min. After one h at 60 – 65 °C the mixture was cooled to room temperature and water (100 ml) was added. Extraction with methylene chloride, washing the organic phase with water (2 × 20 ml), drying and evaporation gave 1.60 g of crude product. Preparative TLC (light petroleum/ether, 3:1) gave 1.0 g, 37 %, of *2c*. MS: 274 (M^+), 243, 173. ^{1}H NMR ($CDCl_3$): δ 3.95 (6 H, s), 7.7 – 8.2 (4 H, m).

Ethoxycarbonylation of 2-methyl-1,4-naphthoquinone. To the vigorously stirred solution of 2-methyl-1,4-naphthoquinone (1.72 g, 0.01 mol), potassium salt of monoethyl oxalate (2.34 g, 0.015 mol), silver nitrate (0.5 g) in acetonitrile (20 ml), and water (20 ml) at 80 °C was added ammonium peroxydisulfate (3.42 g, 0.015 mol) in water (25 ml) during 10 min. After 45 min at 80 °C the mixture was cooled to room temperature and water (50 ml) was added. Extraction with methylene chloride, washing with water (2 × 20 ml), drying (Na_2SO_4), and evaporation gave an oily liquid (2.3 g). Chromatography of the product on silica gel (light petroleum/ether, 4:1) gave three fractions. The first fraction (oil, 120 mg) consisted mainly of 2-methyl-3-ethyl-1,4-naphthoquinone *4a* proved by MS and comparison with an authentic specimen. The second fraction (major, 1.1 g) consisted of *4b* contaminated by some *5a* (MS). *4b* was recrystallized from methanol, m.p. 92 °C. (Found: C 68.97; H 5.03. Calc. for $C_{14}H_{12}O_4$: C 68.85, H 4.91 %). ^{1}H NMR ($CDCl_3$): δ 1.42 (3 H, t, J 6.2 Hz), 2.19 (3 H, s), 4.46 (2 H, q, J 6.2 Hz), 7.6 – 8.2 (4 H, m). The third fraction (360 mg) was impure.

Methoxycarbonylation of 2-methyl-1,4-naphthoquinone. The reaction was analogous to the ethoxycarbonylation. The crude product (2.0 g, from 1.7 g of naphthoquinone) gave by chromatography as the first fraction *4c* (200 mg, somewhat impure) and as the second fraction *4d* (1.7 g, slightly contaminated by *5b*) yellow crystals, m.p. 70 °C (methanol). (Found: C 67.16. H 4.53. Calc. for $C_{13}H_{10}O_4$: C 67.82; H 4.34 %), *5b* was further purified by chromatography, oily liquid. ^{1}H NMR ($CDCl_3$): δ 1.65 (3 H, s), 3.70 (3 H, s), 3.85 (3 H, s), 7.6 – 8.2 (4 H, m), 14.8 (1 H, s).

2-Benzyl-1,4-naphthoquinone, 2d, m.p. 93 °C (lit.[15] 94 °C) was obtained in a yield of 64 % from 1,4-naphthoquinone and phenylacetic acid (1:1.4) at 70 °C in acetonitrile/water, 1:2, as solvent.[1] Small amounts of *2,3-dibenzyl-1,4-naphthoquinone 2e* were formed as a by-product, identical to a specimen prepared by further radical benzylation of *2d* according to the same method (2 equiv. of phenylacetic acid); yield of *2e:* 60 %, yellow crystals, m.p. 80 °C. MS: (M^+) 338. (Found: C 84.40, H 5.43. Calc. for $C_{24}H_{18}O_2$: C 85.20; H 5.32 %). ^{1}H NMR ($CDCl_3$): δ 4.08 (4 H, s), 7.20 (10 H, br.s), 7.5 – 8.2 (4 H, m).

2-(3'-4'-dimethoxy)-benzyl-1,4-naphthoquinone, 2f, was prepared according to the same method,[1] yellowish-brown needles from methanol, m.p. 114 °C, yield 33 %. (Found: C 73.99, H 5.28. Calc. for $C_{19}H_{16}O_4$: C 74.02, H 5.19 %). ^{1}H NMR ($CDCl_3$): δ 3.88 (8 H, br.s), 6.60 (1 H, t, J 1.7 Hz), 6.81 (3 H, br.s), 7.6 – 8.2 (4 H, m).

2-Benzyl-3-ethyl-1,4-naphthoquinone, 8, was prepared in the usual manner from 2-benzyl-1,4-naphthoquinone (0.62 g, 2.5 mmol), propionic acid (0.37 g, 5 mmol), silver nitrate (0.2 g), and ammonium peroxydisulfate (1.14 g,

5 mmol) in acetonitrile (20 ml) and water (40 ml) at 70–80 °C. TLC (silica, CH_2Cl_2) of the crude reaction product gave three fractions: 1, (top fraction) *2g*, 33 mg. 2, 2-benzyl-3-ethyl-1,4-naphthoquinone (460 mg, viscous liquid, 66 %). (Found: C 82.42; H 6.00. Calc. for $C_{19}H_{16}O_2$: C 82.60; H 5.79 %). 3, *2e*, 66 mg. The identity of *2g* and *2e* was proved by MS, ^{1}H NMR, and comparison with authentic specimens.

Ethoxycarbonylation of 2-benzyl-1,4-naphthoquinone, 2d, was carried out with 1.4 equiv. of the potassium salt of monoethyloxalate in acetonitrile/water (1:2) at 75–80 °C. Work-up gave a product (10.7 g from 6.2 g naphthoquinone *2d*) that was chromatographed on silica (light petroleum/ether, 3:1). The following fractions were obtained (from 2.73 g): I, *8*, 0.25 g; II, *8*, (*ca.* 80 %) and *2e* (*ca.* 20 %), 0.54 g; III, *8*, (*ca.* 50 %), *2e* (*ca.* 50 %) 0.44 g; IV, *8*, *9*, *2e*, *6a*, *2d*, 0.21 g, impure; V, *6a*, *9*, *2e*, 0.15 g, impure; VI, *6a*, 1.04 g; VII, *9*, 0.1 g, impure. From VI *6a* was purified by recrystallization in methanol, m.p. 80 °C. (Found: C 75.09; H 5.09. Calc. for $C_{20}H_{16}O_4$: C 75.00; H 5.00 %). ^{1}H NMR ($CDCl_3$): δ 1.34 (3 H, t, J 7.0 Hz), 3.91 (2 H, s), 4.46 (2 H, q, J 7.0 Hz), 7.1–7.5 (5 H, m), 7.6–8.2 (4 H, m). From VII a small amount of *9* crystallized on standing, m.p. 109–110 °C (from methanol). MS: (M+) 394.

Methoxycarbonylation of 2-benzyl-1,4-naphthoquinone, 2d, gave 2-benzyl-3-methoxycarbonyl-1,4-naphthoquinone, m.p. 89 °C (methanol) in a yield of 53 % by chromatography of the crude product, obtained according to the method above. The crude product contained *ca.* 20 % of 2-benzyl-3-methyl-1,4-naphthoquinone. (Found: C 74.31; H 4.79. Calc. for $C_{19}H_{14}O_4$: C 74.50; H 4.57 %). ^{1}H NMR ($CDCl_3$): δ 3.91 (5 H, s), 7.1–7.3 (5 H, br.s), 7.6–8.1 (4 H, m).

Benzylation of juglone acetate. Juglone *10a* was acetylated according to Thomson's procedure.[16] The benzylation procedure for the preparation of 2-benzylnaphthoquinone was followed. The product was recrystallized from benzene and gave 48 % of 3-benzyljuglone acetate *10d*, m.p. 174–175 °C. (Found: C 74.05; H 4.59. Calc. for $C_{19}H_{14}O_4$: C 74.50; H 4.57 %). MS: (M+) 306. ^{1}H NMR ($CDCl_3$): δ 2.48 (3 H, s), 3.83 (2 H, d, J 1.6 Hz), 6.48 (1 H. t, J 1.8 Hz), 7.1–8.1 (8 H, m).

3-Bromojuglone, 10b, and *2 3,6-tribromojuglone* were prepared according to literature.[16,17]

2-Benzyl-3-bromojuglone, 10e, was prepared from *10b* (0.25 g, 1 mmol), phenylacetic acid (0.20 g, 1.5 mmol), and silver nitrate (0.1 g) in acetonitrile (30 ml) and water (40 ml) at 75–80 °C by addition of ammonium persulfate (0.34 g, 1.5 mmol) in water (10 ml). Usual work-up and recrystallization from methanol gave *10e* (0.17 g), m.p. 135 °C. ^{1}H NMR ($CDCl_3$): δ 2.9 (OH, s), 4.25 (2 H, s), 7.2–7.9 (8 H, m).

3-Benzyljuglone, 10f, was obtained by refluxing *10d* (280 mg) in ethanol (35 ml) containing concentrated sulfuric acid (0.5 ml) for 1 h. Half of the solvent was evaporated and water was added. The precipitate was pure *10f* (250 mg, 89 %), m.p. 165 °C. ^{1}H NMR ($CDCl_3$): δ 3.91 (2 H, d, J 1.5 Hz), 6.62 (1 H, t, J 1.5 Hz), 7.1–7.65 (9 H, m), 12.0 (1 H, s).

2-Methoxycarbonyl-3-bromojuglone, 10g, was prepared from *10b* by methoxycarbonylation in the usual way, m.p. 151 °C. ^{1}H NMR ($CDCl_3$): δ 4.01 (OCH_3, s), 7.2–7.8 (3 H, m), 11.8 (OH, s).

Reaction of 2-benzyl-3-ethoxycarbonyl-1,4-naphthoquinone, 6a, with potassium hydroxide. 6a (200 mg) in ethanol (10 ml) was reacted under nitrogen with aqueous potassium hydroxide (20 ml, 4 N) for 24 h. The solution was neutralized with hydrochloric acid, extracted with chloroform, and evaporated. The crude product (190 mg) gave *12* (140 mg) on crystallization from ethanol, m.p. 110 °C. (Found: C 70.67; H 5.38. Calc. for $C_{20}H_{18}O_5$: C 71.00, H 5.32 %). UV (EtOH): λ_{max} 214 (ε 4.42), 237 (4.27), 329 (3.95). IR ($CHCl_3$): 1660, 1620, 1550 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.43 (3 H, t, $J_{AX}=J_{BX}$ 7.07 Hz, ABX_2 system), 3.05 (2 H, s), 4.35 (2 H, $J_{AB}=-10.74$ Hz, $\Delta\nu_{AB}$ 9.17 Hz). 6.6–8.0 (9 H, m), 16.6 (1 H, s).

Reduction of 2-benzyl-3-ethoxycarbonyl-1,4-naphthoquinone, 6a (200 mg) was reduced with Zn dust (2 g) in acetic acid (20 ml) with vigorous stirring for 4 h. Filtration, addition of water, extraction with carbon tetrachloride, washing with aqueous sodium bicarbonate and evaporation gave *13* (180 mg), m.p. 153 °C (from acetonitrile). ^{1}H NMR ($CDCl_3$): δ 1.09 (3 H, t, J 7.2 Hz), 4.26 (2 H, q, J 7.2 Hz), 4.62 (2 H, s), 7.13 (5 H, s), 7.6 (2 H, m), 8.3 (2 H, m). *13* is reoxidized by air to *6a* in alkaline solution.

Reaction of 2-benzyl-3-ethoxycarbonyl-1,4-naphthoquinone with acetic anhydride in acetic acid. 6a (70 mg) was refluxed in acetic acid (1 ml) with acetic anhydride (0.2 ml), and concentrated sulfuric acid (3 drops) for 4 h. The reaction flask was cooled and water (10 ml) was added. Extraction with methylene chloride and chromatography on a TLC plate (light petroleum/ether, 80:20) gave *14* (25 mg), m.p. 191 °C. IR (KBr): 1760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.03 (3 H, s), 2.57 (3 H, s), 6.32 (1 H, s), 7.0–8.1 (9 H, m).

Reduction of 2-benzyl-3-bromojuglone to 10c and 11. 10e (1 g) in acetic acid (30 ml) was stirred with Zn dust (4 g) at reflux temperature for 1 h. The product was filtered and directly oxidized with chromic acid (1 g) for 1 h at 25 °C. Evaporation of half the solvent *in vacuo*, addition of water, extraction with carbon tetrachloride, washing the combined organic phases with saturated sodium bicarbonate, and evaporation gave a mixture of *10c* and *11* (0.43 g). *11* (200 mg) was separated by recrystallization from acetonitrile as yellow crystals, m.p. 159–160 °C. (Found: C 76.57; H 5.30. Calc. for $C_{17}H_{14}O_3$: C 76.69; H 5.26 %). ^{1}H NMR ($CDCl_3$): δ 2.6–3.5 (5 H, m), 7.2–7.7

(8 H, m), 13.9 (1 H, s). From the filtrate *10c* (130 mg, red crystals), m.p. 98 °C, and a mixture of *10c* and *11* (40 mg) was isolated by preparative TLC (SiO_2, CH_2Cl_2, closely lying bands). ^1H NMR ($CDCl_3$): δ 3.89 (2 H, d, J 1.5 Hz), 6.57 (1 H, t, J 1.5 Hz), 7.3 (6 H, m), 7.6 (2 H, m).

When *11* was dissolved in dilute aqueous base, aerated for a short time, acidified, and worked-up, the ^1H NMR spectrum of the crude product showed *10c* as major product.

Cyclization of 6a with polyphosphoric acid (PPA). Preparation of the naphthacene quinone 15. *6a* (100 mg) was heated for 4 h at 100 °C in PPA (3 g) under N_2. Crushed ice was added after cooling of the dark coloured mixture to room temperature. The finely divided precipitation was allowed to settle, filtered, and washed with water. Recrystallization from hot toluene gave *15* (30 mg) red needles, m.p. 310–311 °C (lit.[18] 310 °C). MS (M^+) 274. Cyclization of the corresponding methyl ester (0.5 g) according to the same procedure gave *15* (0.2 g).

The semiquinone radicals were generated in water/ethanol (1:1), 0.01 M sodium hydroxide, by reduction of the quinones with sodium dithionite.

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