Alkylation of Quinones by Carbanions: Use of Pyridinium Ylides to insert Phenacyl, Acetonyl and Related Groups

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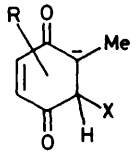
Reports that carbanions C^- add to quinones Q in the ratios 1 : 1 and 2 : 1 are confirmed; even if an excess of quinone is present, cage or bridge products are formed only if the carbanion is itself quinonoid. Pyridinium salts $C_5H_5\overset{+}{N}CH_2COR\ X^-$ react with quinones in mildly basic solvents to give acetonylquinones and other quinones containing the group $RCOCH_2$.

Quinones have long been known to add nucleophiles (in particular, carbanions) as in Michael reactions leading in the first place to anionic intermediates of type (1) and then by protonation, enolisation, and oxidation to the products, quinols (2) or substituted quinones (3).[1] Alternatively, the use of a chloroquinone allows the product to be formed by halide elimination as in (4). Such later steps may be supposed to be fast enough to make detection of the intermediate anion (1) rather difficult, yet when the carbanion (5) adds to 2,5-dimethyl-1,4-benzoquinone the corresponding intermediate (6) lasts long enough to be intercepted by another benzoquinone molecule, thus producing the cage tetraketone (7) and related compounds.[2] It is, therefore, necessary to know whether such reactions are special cases, or whether they are general, but have been overlooked in earlier work. For this reason we have repeated a number of known reactions except that an excess of the quinone was used to increase the likelihood of cage or bridge formation. In every example we confirmed the published reports and failed to find any cage product and are, therefore, led to conclude that cage formation is indeed rare, or at least not general. Special consideration was given to cyanide,[3] anions from alkyl malonates,[4] and indan-1,3-dione,[5] but only novel results are reported here. In a new extension the use of pyridinium ylides was found to provide a convenient method of introducing acetonyl and similar residues into quinone nuclei.

2-Methyl-1,4-naphthoquinone adds nitromethane in base to give the methylenebisnaphthoquinone (8); probably the simple adduct (9) is formed first and then, since it possesses a highly activated methylene group, it loses a proton and another quinone molecule adds, the sequence being completed by elimination of nitrite ion as in (10) giving a quinone methide that tautomerises. Ethyl malonate anion was found to add readily, but messily in accord with previous observations.[6]

In the course of other studies, we have used the addition of ethyl 3-oxobutanoate to quinones for synthetical purposes, as described by Eugster and his colleagues,[7] and later by Coombes.[8] Like them, we found that the yields are often very good and that the stoicheiometry is 1 : 1 and cage or bridge ketones are not formed.

Indan-1,3-dione (11) was examined because its anion is in a sense a diminished vinylogue of the carbanion (5). Even so, it gave no cage ketones. The reaction between the indandione and 2-methyl-1,4-naphthoquinone in ethanol was very slow until pyridine was added and even then the mixture had to be heated to give the 1 : 1 reaction product (12). This compound was troublesome to purify and characterise, probably because it can exist in several tautomeric forms of similar stability. The more reactive 2,5-dimethyl-1,4-benzoquinone did not require heating and gave mainly the 1 : 1 product (13) with some of the 1 : 2 product (14).



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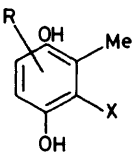

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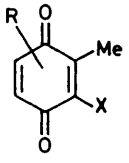

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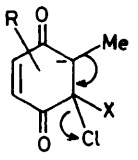

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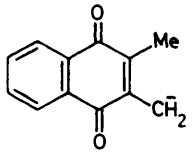

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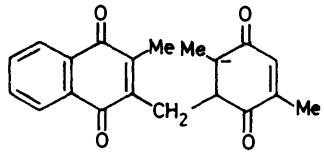

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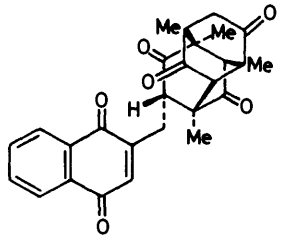
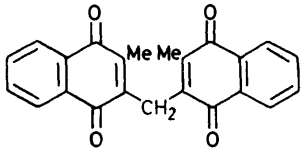


(7)

Buggle *et al.*,[9] allowed 1,4-naphthoquinone to react with 2-acetylindan-1,3-dione in hot ethanol and obtained the 1 : 1 product (15) along with a very small amount of a 2 : 1 product, to which they ascribed structure (16) on the basis of very limited evidence. It seemed to us that this substance might have had a cage or bridge structure, but when we repeated the experiments we could find only the major product (15).

The preparation of pyridinium salts (17) [10] and their ability to form nitrogen ylides [11] under very mild conditions (not inimical to quinones) are well documented. The ylides were produced *in situ* by means of triethylamine in methanol or ethanol as a rule, but better results were obtained in a two-phase system with the quinone in dichloromethane or tri-



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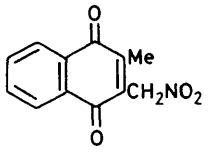

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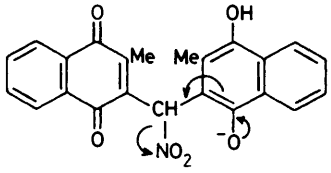

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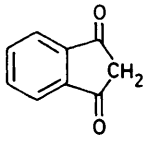

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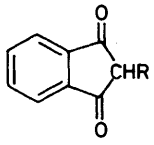
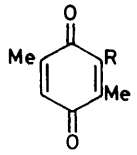


(12)

R = 3-methyl-1, 4-dioxo-2-naphthyl



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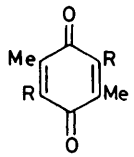
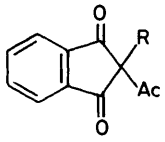


(14)

R = 1, 3-dioxoindan-2-yl



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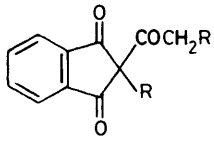


(16)

R = 3-methyl-1, 4-dioxo-2-naphthyl

chloromethane. Further improvement was secured for naphthoquinones by using an aprotic solvent. Dichloromethane or trichloromethane were used with a pyridinium iodide, potassium carbonate, and a crown ether. Acetonitrile was used with a pyridinium bromide and triethylamine. In general, the reaction is considered to take the course shown in the Scheme. As far as quinol formation the steps are expected ones, and the elimination of pyridine leaving a quinone methide has close parallels.[12] The electronic interaction in the quinone methide presumably both assists the elimination and stabilises the quinonoid system against the self-condensation characteristics of members of the group lacking the acyl group.[12,13] The reactions studied are listed in Tables 1 and 2, and the structure of 2-phenacyl-3,5,6-trimethyl-1,4-benzoquinone (18a) was confirmed by condensing the compound with hydrazine to form the phenolic cinnoline derivative (19). Yields were usually good except with 2,5-dimethyl-1,4-benzoquinone, which gave a mixture of the mono-substituted (18b) and the di-substituted quinone (20), as well as a substance believed to have structure (21). Such a product is to be expected from photodimerisation of the monosubstituted quinone (18b), except that only in this experiment was a dimer formed and that there are strong parallels with a 2 + 2 dienone cycloaddition we have previously surmised might occur under the influence of a tertiary amine, rather than simply by the action of light.[14]

Experimental

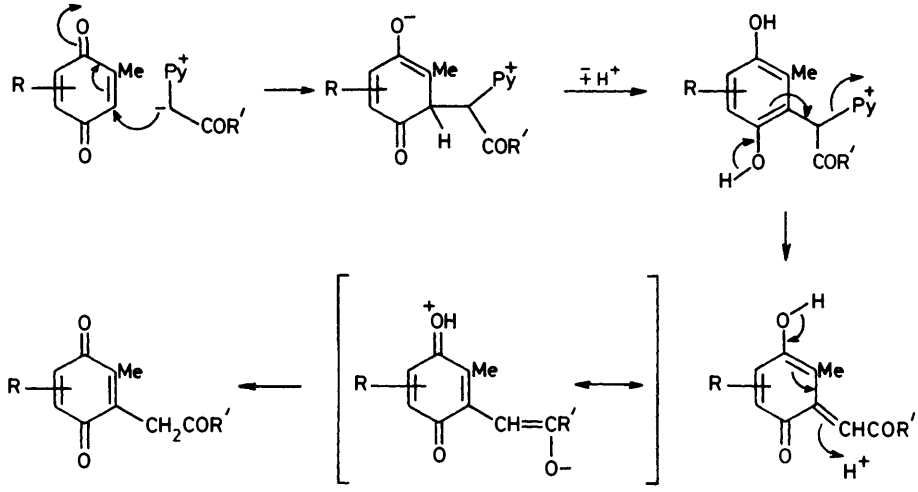
U.v. spectra were determined on *ca.* 10^{-3}M-solutions in ethanol using a Pye Unicam SP8-100 u.v. spectrometer. I.r. spectra were recorded on a Perkin-Elmer 125 i.r. spectrometer. N.m.r. spectra were generally recorded at 220 MHz on a Perkin-Elmer R34 machine. Molecular weights were determined mass spectroscopically.

2-Methyl-1,4-naphthoquinone and Nitromethane.—Nitromethane (5 ml) containing 2-methylnaphthoquinone (0.34 g) was added to methanol (10 ml) containing dissolved sodium metal (0.025 g). After 1 h the yellow precipitate was collected and found to consist solely of 3,3′-dimethyl-2,2′-methylenedi-1,4-naphthoquinone (8) (0.08 g), m.p. 270 °C (decomp.), identified spectroscopically by comparison with an authentic specimen.

The Reaction of Indan-1,3-dione with 2-Methyl-1,4-naphthoquinone.—2-Methylnaphthoquinone (172 mg) and indandione (73 mg) were heated together in refluxing ethanol (5 ml) containing pyridine (four drops) for 7 h. The solution was cooled, acidified with dilute hydrochloric acid, and concentrated until crystallisation began. The yellow solid was purified from ethanol to give 2-(1,3-dioxoindan-2-yl)-3-methyl-1,4-naphthoquinone (12) as a *hemihydrate* (90 mg), m.p. 230—232 °C, $\lambda_{max.}$ 251, 258sh, 313, and 325 nm (log ε 4.48, 4.42, 3.64, and 3.51); $\nu_{max.}$ 1 742, 1 709, and 1 705 (indan-1,3-dione system), 1 645, 1 618, and 1 585 cm^{-1} (1,4-naphthoquinone system); δ 2.40 (3 H, s, Me), 4.36 (1 H, s, at once exchanged by D_2O, methine CH), 7.7 (2 H, mm, ArH), 7.9 (3 H, mm, ArH), and 8.1 (3 H, mm, ArH) (Found: C, 73.3; H, 3.8%. $C_{20}H_{12}O_4 \cdot 0.5H_2O$ requires C, 73.8; H, 3.7%). The compound retains the water of crystallisation strongly, but the mass spectrum corresponded to the anhydrous material (Found: *m/z* ($M^{+\cdot}$ 316). $C_{20}H_{12}O_4$ requires *m/z* ($M^{+\cdot}$) 316.

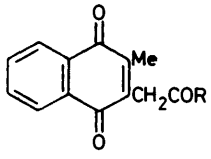
An attempt was made to induce addition to methylnaphthoquinone by treating the indandione in tetrahydrofuran at −70 °C with butyl-lithium in hexane and adding the quinone. After 15 min, the mixture was flooded with dilute hydrochloric acid, but most of the quinone was recovered and only traces of the adduct were detected by t.l.c.

The Reaction of Indan-1,3-dione with 2,5-Dimethyl-1,4-benzoquinone.—(i) *With Sodium Hydroxide.* Dimethylquinone (544 mg) and indandione (292 mg) in methanol (20 ml) were treated with 0.1M-sodium hydroxide (0.5 ml) at room temperature for 20 min. The mixture was acidified with dilute hydrochloric acid and the products isolated by extraction into trichloromethane. When concentrated and kept for a time, the extract deposited dimethylquinone (120 mg). The mother liquor was diluted with ether and extracted with saturated aqueous sodium hydrogen carbonate. The aqueous layer was acidified and the product isolated by means of trichloromethane and purified from ethanol giving 2-(3,6-*dimethyl*-2,5-*dioxophenyl*)*indan*-1,3-*dione* (13) as irregular, yellow prisms (240 mg), m.p. 149—150 °C, $\lambda_{max.}$ 234, 254, 296, and 298 nm (log ε 4.26, 4.36, 3.71, and 3.66), $\nu_{max.}$ 1 750, 1 715, and 1 705



Scheme.

Table 1. Derivatives (22) of 2-methyl-1,4-naphthoquinone



Structure no.	R	Yield (%)	Method	^{1}H N.m.r. δ(CDCl$_3$) at 220 MHz: Quinone protons 5,8	6,7	Me	CH_2	Substituent (R) protons: Ar 2,6	Ar 3,5	Ar 4	Me (OMe)	CH_2 (OCH_2)
(22a)	Ph	65	A	8.00	7.65	2.10	4.33	8.00	7.47	7.35		
(22b)	4-$NO_2C_6H_4$	85	B	8.00	7.67	2.12	4.32	8.16	8.31			
		80	A	(1 H) 8.06 (1 H)								
(22c)	Me	60	A	8.09	7.70	2.12	3.81				2.30	
(22d)	OMe	55	A	8.10	7.70		3.73				3.70	
(22e)	OCH_2Me	55	A	8.10	7.70	2.21	3.75				1.28 (5, *J* 7 Hz)	4.20 (q, *J* 7 Hz)
		80	B									

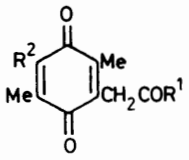
(indandione system), 1 645, 1 630, and 1 612 cm^{-1} (benzoquinone system), δ 1.92 (3 H, d, *J ca.* 2 Hz, CH:CC*H*$_3$), 2.23 (3 H, s, other quinone Me), 4.25 (1 H, s, not exchanged by D_2O, CO.CHR.CO), 6.67 (1 H, q, *J ca.* 2 Hz, quinone CH), 7.9 and 8.2 (each 2 H, mm, ArH) [Found: C, 72.8; H, 4.45%; *m/z* (*M*$^{+\cdot}$) 280 (but *M* + 2 peak is stronger). $C_{17}H_{12}O_4$ requires C, 72.8; H, 4.3%; *m/z* (*M*$^{+\cdot}$) 280].

(ii) *With pyridine.* A solution of indandione (73 mg), dimethylquinone (136 mg), and pyridine (2 drops) in ethanol (5 ml) was kept at *ca.* 20 °C in the dark for four days. Yellow crystals separated; we could not find a solvent for recrystallisation so the solid was thoroughly washed with ethanol and identified as 2,2′-(3,6-dimethyl-2,5-dioxo-*p*-phenylene)bisindan-1,3-dione as a *hemihydrate* (14), m.p. >320 °C, $\lambda_{max.}$ ($CHCl_3$) 254 nm (log ε 4.65); $\nu_{max.}$ 1 742, 1 715 and 1 708 (indandione system), 1 645, 1 638, and 1 615 cm^{-1} (benzoquinone system); δ($CDCl_3$ + $F_3C.CO_2H$) 2.12 (6 H, s, Me), 4.32 (2 H, s, COCHRCO), 7.98 (4 H, mm, ArH), and 8.09 (4 H, mm, ArH) (Found: C, 71.85; 71.9; H, 3.9; 3.9. $C_{26}H_{16}O_6 \cdot 0.5H_2O$ requires C, 72.0; H, 4.2%). The mass spectrum corresponded to the anhydrous compound (Found: *M*$^{+\cdot}$, 424. $C_{26}H_{16}O_6$ requires *M*, 424).

The mother liquors were concentrated and left in contact with dilute hydrochloric acid for 12 h. A red solid was obtained; several crystallisations some from benzene and some from ethanol supplied the indandione (13) along with dimethylbenzoquinone and its quinol. T.l.c. indicated no other components of the mixture.

The Reaction of 2-Acetylindan-1,3-dione with 1,4-Naphthoquinone.—1,4-Naphthoquinone (632 mg) in ethanol (10 ml) and 2-acetylindan-1,3-dione (118 mg) were heated together under reflux for 48 h. When the reaction mixture was concentrated and allowed to stand it deposited a dirty green product which appeared to be a quinhydrone; this was collected and warmed with iron(III) chloride in methanol for 5 min. The product crystallised from ether–methanol and then benzene to give 2-(2-acetyl-1,3-dioxoindan-2-yl)-1,4-naphthoquinone[9] (15) as small yellow crystals (206 mg), m.p. 188—190 °C, $\lambda_{max.}$ 1 775, 1 740, 1 705 (indandione system), 1 660, 1 615 and 1 585 cm^{-1} (naphthoquinone system); δ 2.36 (3 H, s, Me), 6.49 (1 H, s, quinone CH), 7.6—7.7, 7.75—7.9, and 7.95—8.1 (8 H, mm, ArH) (Found: C, 75.1; H, 4.2. Calc. for $C_{21}H_{12}O_5 \cdot 0.5C_6H_6$: C, 75.0; H, 3.9%). The

Table 2. Derivatives of 2,5-dimethyl-1,4-benzoquinone

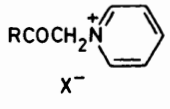


Proton	δ-Values (CDCl₃ at 220 MHz) Aromatic 2,6	3,5	4	CH_2	Quinone Me			Yield Method A %	Method B %
R^2 = Me, R^1 = Ph	8.03	7.51	7.60	4.23	2.04	2.01	2.01	40	60
R^2 = Me, R^1 = Me				3.63	2.01	2.00	1.96 *	50	
R^2 = CH_2COPh, R^1 = Ph	8.03	7.55		4.25	2.10	2.00		20	20

* Acetonyl Me, δ = 2.25.

Table 3. Pyridinium salts (17) ^1H n.m.r. spectra, δ[$(CD_3)_2SO$] at 220 MHz

R	X^-	M.p.	Pyridine ring 2	3	4	$CH_2\overset{+}{N}$	Ar 2,6	3,5	4	Me	OCH_2–
Ph	I	218	9.12	8.40	8.86	6.90	8.18	7.77	7.90		
4-$NO_2C_6H_4$	I	213	9.04	8.50	8.79	6.57	28.3	28.3			
Me	I	201	9.08	8.28	8.72	6.03				2.36	
OEt	Br	134	9.18	8.30	8.77	5.8				1.26 (t, *J* 7 Hz)	4.26 (q, *J* 7 Hz)



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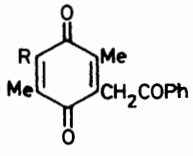
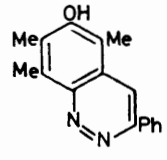


(18)

a; R = Me

b; R = H



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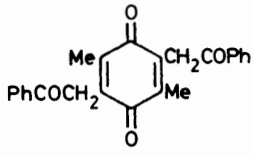

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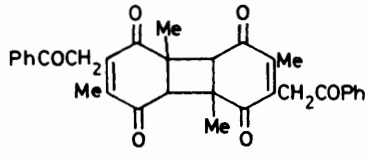

(21)

mass spectrometer showed the solvent-free molecular ion at *m/z* 344. Calc. for $C_{21}H_{12}O_5$: *m/z* ($M^{+\cdot}$) 344.

Pyridinium Salts.—These were known compounds prepared according to literature methods. Their ^1H n.m.r. spectra are listed in Table 3.

Reaction of 2-Methyl-1,4-naphthoquinone with Phenacylpyridinium Iodide (Method A).—The phenacylpyridinium iodide (0.33 g) in methanol (15 ml) was treated with triethylamine (0.14 ml) for 2 min and then 2-methylnaphthoquinone (0.17 g) was added and the mixture stirred for 24 h. The resulting solution was diluted with dichloromethane and washed with dilute hydrochloric acid. The organic layer provided a solid which was chromatographed on silica from benzene; the first fractions contained methylnaphthoquinone, later fractions contained *2-methyl-3-phenacyl-1,4-naphthoquinone* (22a) which separated from ethanol as yellow needles (0.2 g), m.p. 112—115 °C, $\nu_{max.}$ 1 674 (phenacyl C:O), 1 655, 1 622 and 1 590 (naphthoquinone system), 752, 710, 690 (aromatic) [Found: C, 78.7; H, 5.0%; *m/z* ($M^{+\cdot}$) 290. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.8%; *m/z* ($M^{+\cdot}$) 290]. In a similar reaction, phenacylpyridinium bromide (0.28 g) was suspended in acetonitrile (10 ml) containing 2-methylnaphthoquinone (0.17 g). Triethylamine (1 equiv.) was added after the apparatus had been purged with nitrogen and the mixture was stirred for 24 h. Solvent removal provided a brown solid which, after preparative thin-layer chromatography [silica, dichloromethane–light petroleum (b.p. 60—80 °C) (1 : 1)] gave *2-methyl-3-phenacyl-1,4-naphthoquinone* (22a) (0.20 g) (69%).

2-Methyl-3-(4-nitrophenacyl)-1,4-naphthoquinone (22b).—Prepared from 4-nitrophenacylpyridinium iodide (0.35 g) and 2-methylnaphthoquinone (0.17 g by Method A), this *nitrophenacylquinone* separated from ethanol as yellow prisms (0.27 g), m.p. 165—166 °C, $\nu_{max.}$ 1 690 (phenacyl C:O), 1 664, 1 630 and 1 590 (naphthoquinone system), 1 600 (aromatic), 1 512 (nitro), 749, 728 and 700 cm^{-1} (aromatic) [Found: C, 67.95: H, 4.1%; N, 4.18%; *m/z* ($M^{+\cdot}$) 335. $C_{19}H_{13}NO_5$ requires C, 68.1; H, 3.9; N, 4.2%; *m/z* ($M^{+\cdot}$) 335].

2-*Acetonyl*-3-*methyl*-1,4-*naphthoquinone* (22c).—The interaction between acetonylpyridinium iodide (0.34 g) and methylnaphthoquinone (0.34 g) in ethanol (5 ml) containing triethylamine (0.28 g) threw down a solid after a few minutes and was terminated after 1 h. The product was isolated as in the preceding examples, but very little methylnaphthoquinone was retrieved and chromatography was hardly necessary. The yellow *acetonylquinone* (0.31 g) was purified from ethanol and had m.p. 130—131 °C, $\nu_{max.}$ 1 708 (acetonyl C:O), 1 660, 1 621 and 1 590 (naphthoquinone system), and 710 cm^{-1} (aromatic) (Found: C, 73.9; H, 5.4%; $M^{+\cdot}$, 228. $C_{14}H_{12}O_3$ requires C, 73.7; H, 5.3%; *M*, 228).

Ethyl 3-*Methyl*-1,4-*dioxo*-2-*naphthylacetate* (22e).—Obtained from ethoxycarbonylmethylpyridinium bromide (0.25 g) and 2-methyl-naphthoquinone (0.17 g) in methanol by Method A, *methyl* 3-*methyl*-1,4-*dioxo*-2-*naphthylacetate* (22d) separated from ethanol as yellow rhombs (0.12 g), m.p. 112—114 °C, $\nu_{max.}$ 1 730 (ester), 1 660, 1 612 and 1 588 (naphthoquinone system), and 690 cm^{-1} (aromatic) [Found: C, 69.0; H, 4.9%; *m/z* ($M^{+\cdot}$) 244. $C_{14}H_{12}O_4$ requires C, 68.8; H, 4.9%; *m/z* ($M^{+\cdot}$) 244]. When the reaction solvent was ethanol, the product was the expected *acetate* (22e), m.p. 90 °C, $\nu_{max.}$ 1 715 (ester), 1 662, 1 625 and 1 590 (naphthoquinone system) and 700 cm^{-1} (aromatic) [Found: C, 70.0; H, 5.4%; *m/z* ($M^{+\cdot}$) 258. $C_{15}H_{14}O_4$ requires C, 69.75; H, 5.5%; *m/z* ($M^{+\cdot}$) 258].

The Reaction of Pyridinium ylides with Quinones: *Method B*.—The pyridinium salt (10^{-3} mol) was suspended in dichloromethane (5 ml) containing (for example) 2-methyl-1,4-naphthoquinone (2×10^{-3} mol), potassium carbonate (10^{-3} mol), and a catalytic amount of 18-crown-6 ether (2—3 mg). The mixture was stirred for 10 h, diluted with dichloromethane, and washed with dilute hydrochloric acid. The product was isolated in the usual way and chromatographed on silica from benzene to give the substituted quinones. Yields are indicated in Tables 1 and 2.

2,5,6-*Trimethyl*-3-*phenacyl*-1,4-*benzoquinone* (18a).—The reaction of trimethylbenzoquinone (0.15 g) with phenacylpyridinium iodide (0.33 g) in methanol containing triethylamine (0.14 ml) as in Method A was allowed to continue for 24 h. Chromatography on silica from light petroleum–dichloromethane gave as the main fraction a very viscous mass which failed to crystallise from common solvents until a hexane solution was left at 5 °C for several days. Obtained in this way, the *phenacylbenzoquinone* formed yellow *nodules* (0.11 g), m.p. 95 °C, $\nu_{max.}$ 1 682, 1 640, 1 630, 1 590, and 710 cm^{-1} [Found: C, 75.9; H, 6.1%; *m/z* ($M^{+\cdot}$) 268. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%; *m/z* ($M^{+\cdot}$) 268]. A better yield (60%) was obtained by the use of Method B.

6-*Hydroxy*-5,7,8-*trimethyl*-3-*phenylcinnoline* (19).—The phenacylquinone (18a) (0.26 g), hydrazine hydrate (0.05 ml), and acetic acid (two drops) were dissolved in toluene (sodium-dry; 5 ml) and kept for 18 h. The resulting slurry was diluted with dichloromethane and washed with buffer solution at pH 3.28. The organic layer yielded a light yellow solid mixture from which ether removed several components leaving insoluble material. This was difficult to crystallise, but separated from toluene as a powder (60 mg) identified as the *cinnoline*, m.p. 266 °C, $\lambda_{max.}$ (5 mg l^{-1} in EtOH) 273 nm (log ε 4.64); $\nu_{max.}$ 3 030br (H-bonded OH), 1 590, 1 582 and 760 cm^{-1}; δ[$CDCl_3$ + $(CD_3)_2SO$], 2.47, 2.53 and 2.96 (each 3 H, s, Me), 2.90br (1 H, removed by D_2O, OH), 7.55 (3 H mm, *meta* and *para* ArH), 8.12 (1 H, s, cinnoline nucleus), and 8.25 (2 H, d, ArH *ortho* to cinnoline) [Found: C, 77.3; H, 6.25; N, 10.7%; *m/z* ($M^{+\cdot}$) 264. $C_{17}H_{16}N_2O$ requires C, 77.3; H, 6.0; N, 10.6%; *m/z* ($M^{+\cdot}$) 264].

The *acetate*, m.p. 60—62 °C (from ether–hexane), had δ 2.33, 2.42, 2.44 and 3.01 (all 3 H, s, Me), 7.55 (3 H, mm, *meta* and *para* ArH), 8.20 (1 H, s, cinnoline nucleus), and 8.28 (2 H, d, *ortho* ArH).

2-*Acetonyl*-3,5,6-*trimethyl*-1,4-*benzoquinone* (18a; Me for Ph).—Trimethylbenzoquinone (0.30 g) was treated with acetonylpyridinium iodide (0.34 g) by Method A and the reaction terminated after 3 h. Isolated in the usual way, the product formed a yellow syrup that was chromatographed on silica from benzene to give the crude quinone as a viscous mass that crystallised when the hexane solution was kept at 5 °C for several days and so gave the *acetonylquinone* as yellow rhombs (0.15 g), m.p. 53 °C, $\nu_{max.}$ 1 720 and 1 635 cm^{-1} [Found: C, 70.0; H, 7.0%; *m/z* ($M^{+\cdot}$) 206. $C_{12}H_{14}O_3$ requires C, 69.8; H, 6.8%; *m/z* ($M^{+\cdot}$) 206].

2,5-*Dimethyl*-3,6-*diphenacyl*-1,4-*benzoquinone* (20).—2,5-Dimethyl-1,4-benzoquinone (0.14 g) and phenacylpyridinium iodide (0.63 g) were condensed by Method A for 3 h and the product crystallised from methanol to give the *diphenacylquinone* as yellow nodules (0.1 g), m.p. 225—227 °C, $\nu_{max.}$ 1 670, 1 635, 1 590, and 750 cm^{-1} [Found: C, 77.1; H, 5.4%; *m/z* ($M^{+\cdot}$) 372. $C_{24}H_{20}O_4$ requires C, 77.4; H, 5.4%; *m/z* ($M^{+\cdot}$) 372]. The mother liquors were found by spectroscopic and other methods, to contain both this quinone and 2,5-dimethyl-3-phenacyl-1,4-benzoquinone (18b) (but the latter could not be obtained pure), and also photodimer (21).

A similar reaction conducted by Method B also gave a mixture from which only the diphenacylquinone could be obtained pure. The yield was the same.

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