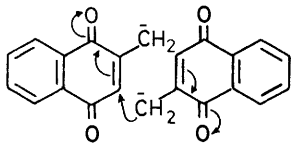
Adducts from Quinones and Diazoalkanes. Part 9.[1] The Adduct from 2-Methyl-1,4-napthoquinone and Diazoethane and the Derived Secondary Carbanion: Regioisomerism in Carbanion–Quinone Additions

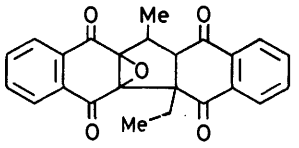
By **Francis M. Dean,* Leonard E. Houghton, Rassoul Nayyir-Mashir,** and **Chachanat Thebtaranonth,** The Robert Robinson Laboratories, The University of Liverpool, Liverpool L69 3BX

Diazoethane adds to 2-methyl-1,4-naphthoquinone giving mainly one regioisomeric pyrazoline (5a) as a mixture of epimers at position 3. The other regioisomer was detected and a related compound (7) was obtained from a similar reaction with diazomethane. The pyrazoline (5a) is transformed into the carbanion (3b) with base and thence into the butylenediquinone (9). Thermal decomposition affords 2-ethyl-3-methyl-1,4-naphthoquinone. Treatment with methanolic base and 2-methyl-1,4-naphthoquinone gives the fluorene derivative (11a) not the expected alcohol (12). Treatment with methanolic base and trimethyl-1,4-benzoquinone affords the expected xanthen derivative (16) but the congeneric fluorene alcohols differed regiospecifically from those observed in other series. One (14) has a *cis*-fused nucleus; the other is believed to be the *trans*-fused analogue (13), another departure from previous experience. On the other hand, the reaction with 2,5-dimethyl-1,4-benzoquinone leads to the cage tetraketone (17a) as expected.

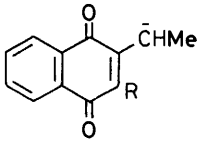
WHEN Baxter *et al.*[2] treated 2-methyl-1,4-naphthoquinone with alkali they obtained a naphthacene derivative clearly formed by way of the double Michael addition indicated in (1) for which there is ample precedence.[3] But 2-ethylnaphthoquinone gave a product [4] (2), apparently derived from carbanion (3a) acting



(1)

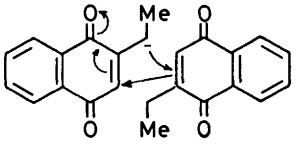


(2)



(3)

a; R = H
b; R = Me
c; R = CH_2Ph



(4)

on a second, neutral quinone as in (4), in a way for which there is no precedent. It might be that the ethyl carbanions differ generally from their methyl analogues (to which earlier studies have been almost entirely confined) so we have extended our work to related ethyl carbanions such as (2b). These do behave somewhat differently from the lower homologues, but we have not observed any condensation like that in (4).

RESULTS AND DISCUSSION

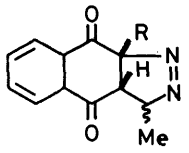
The addition of diazoethane to methylnaphthoquinone gave the desired adduct (5a) as a mixture of epimers (ratio *ca.* 1 : 10) as described earlier [5] (but contrast another report [6]) except that a minor, less soluble fraction appeared to consist of a substance (6a) from the alternative mode of addition. Although such a result is to be expected on theoretical grounds, the minor regioisomers from quinone–diazoalkane additions seem to be unknown as yet.[3,6] Hence we attempted to isolate (6a) but failed, partly because the product is unstable under most conditions and partly because it consists of a mixture of epimers. The second problem does not exist in the diazomethane analogue (6b); and after removal of the major adduct from the addition of diazomethane to methylnaphthoquinone in ether, we were able to isolate from the bright yellow mother-liquor a compound to which we assign structure (7). Presumably the original adduct was (6b) which contains a mobile methine proton liable to migrate during manipulation. Tautomer (7) is chosen rather than any other because it is, in effect, a nitrogen analogue of a (vinylogous) amide and should therefore be comparatively stable. Moreover, it contains a chromophoric system like that in a chalcone, which could also explain the bright yellow colour.

As obtained, the adduct (5a) is a mixture of epimers depending upon the secondary methyl group, but since both epimers yield the same carbanion (3b) when treated with base we did not try to separate them but used the mixture. It might be argued that, since methyl substituents destabilise carbanions, carbanion (3b) should isomerise into carbanion (8); however, we detected no product formed in this way. Previously we reported that adduct (5a) with base in methanol gives a tar; [5] from this we have now obtained the expected diquinone (9) in comparatively poor yield. The product appears to be a single substance but we did not examine it closely and it may be a mixture of stereoisomers. With *N*-methylaniline present, the reaction readily supplied the expected [7a] quinone methide addition product (10), which will be reported separately. In both reactions the initial products should be quinols rather than quinones but we allowed air to oxidise them into the more convenient form. When heated in polar aprotic solvents the adducts (5a) extruded nitrogen (7b) to give 2-ethyl-3-methyl-1,4-naphthoquinone [8] in rather poor yield.

Reactions between carbanion (3b) and quinones can take various routes as summarised in the Scheme.

The reaction between the carbanion (3b) and 2-

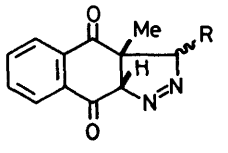
methyl-1,4-naphthoquinone gave a mixture from which only one product could be readily isolated, the yellow fluorene derivative (11a). The i.r. spectrum showed that only conjugated carbonyl groups were present and



(5)

a; R = Me

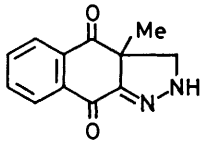
b; R = CH_2Ph



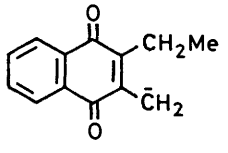
(6)

a; R = Me

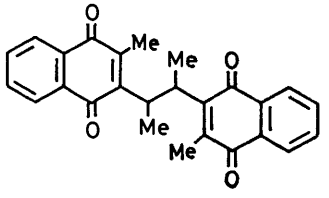
b; R = H



(7)



(8)



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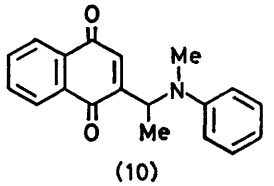
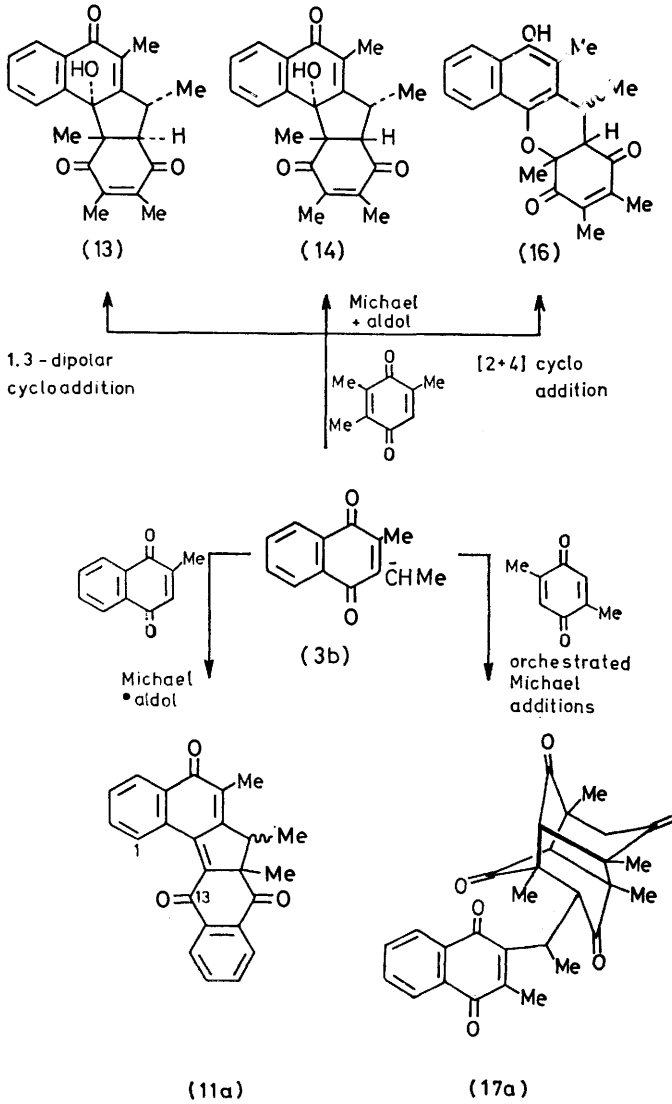


(10)

no hydroxy-group; the ^1H n.m.r. spectrum included the requisite AX_3 spin system and two singlets, one at high field assigned to the angular methyl group, and one at lower field (δ 2.30) assigned to the vinylic methyl group under the influence of electron withdrawal by the distant but conjugated carbonyl group in the other naphthalene residue. A highly characteristic feature was the resonance of the aromatic proton at position 1, which is shifted strongly downfield to δ 8.98 by the deshielding cone of the 13-carbonyl group. Similarly, the diazoethane adduct (5b) from 2-benzylnaphthoquinone and diazoethane was used to generate the carbanion (3c) for reaction with 2-methylnaphthoquinone, and the fluorene derivative (11b) resulted. In these reactions the orientation of addition is that encountered before, the only new feature being the spontaneous elimination of water from the expected products, the alcohols (12).

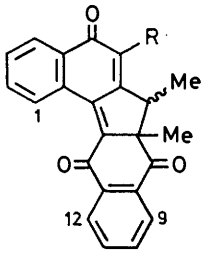
More important is the discovery that, when carbanion (3b) adds to trimethyl-1,4-benzoquinone to form a fluorene derivative, it does so with the alternative regiospecificity. This has not been observed before. The product is a fluorene alcohol (13) that cannot readily undergo dehydration, and both i.r. and n.m.r. methods establish the presence of its hydroxy-group. The i.r. spectrum also contains bands appropriate to ene-dione and to acrylophenone carbonyl groups, while the ^1H n.m.r. spectrum (Table 1) demonstrates the presence of the Me–CH–CH– grouping by appropriate multiplets (J 10 and 7 Hz), confirmed by spin-decoupling experiments. The two ene-dione methyl groups are readily recognised because mutual homoallylic coupling causes them to resonate as quartets (J *ca.* 1.3 Hz) instead of



SCHEME Summary of carbanion–quinone additions, with postulated types of reaction mechanism

singlets. A true singlet appears at δ 0.92 and is assigned to the angular methyl group; another singlet appears at δ 1.79 and is assigned to the remaining vinylic methyl group. Both these shifts have special significance. The

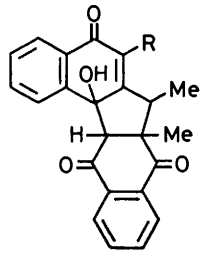
latter shows that there is no longer a carbonyl group at the β-position withdrawing electrons [contrast (11a) above, where the corresponding shift is δ 2.30], and so



(11)

a; R = Me

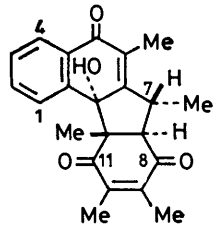
b; R = CH_2Ph



(12)

confirms the location of the alcohol function. The former is unique in these studies; many closely similar angular methyl groups have been examined and found to resonate at no higher fields than δ *ca.* 1.3; models show that each of the surrounding unsaturated groupings can make some contribution to the total anisotropic deshielding.

be *trans*, and the angular methyl group must be *trans* to the hydroxy-group. The derived stereochemistry is indicated in (13); it minimises contributions to anisotropic deshielding by some of the unsaturated units present but, most importantly, it causes the carbonyl group at position 8 to tilt so that it shields the angular methyl group, an effect not present in geometries based on *cis*-fusion. There is an alternative *trans*-fused arrangement that has the hydroxy and angular methyl groups *cis*, but it is ruled out because the methyl group



(13)

would suffer net deshielding, and also particularly because a carbonyl group would project over the benzene ring and greatly alter the resonances there. Arguments

TABLE 1

^{1}H N.m.r. spectra [a] (at 220 MHz) for neutral and acid solutions [b] of various fluorene and xanthen derivatives

	Aromatic											
	ortho or *peri*		Other		Ar-Me	enone-Me	ene-dione-Me_2 [c]	Secondary Me	CH_2 or CHMe	Ring-junction CH	OH [d]	Angular Me
Fluorene (13)	7.95d (8)	7.75m	7.75m	7.42m		1.78	2.08, 2.21	1.41d (7)	3.58dq (10.5 and 7)	3.10d (10.5)	2.8	0.85
With acid [e]	8.08d (8)	7.65m	7.52m	7.52m		2.00	2.10, 2.24	1.38d (7)	3.71dq (10 and 7)	3.28d (10)		0.92
With acid [f]	7.92d (8)	7.55m	7.55m	7.39m		1.78	2.07, 2.21	1.40d (7)	3.59m	3.12d (10)		0.85
Fluorene (14)	7.98d	7.74d	7.59dd	7.40dd		1.71	1.74 1.97	1.52d (7)	2.75dq (7) and 7)	3.38d (7)	2.91	1.62
With acid [e]	8.12d	7.72d	7.65dd	7.50dd		1.84	1.79, 2.02	1.50	3.86dq	3.46d (7)		1.74
Fluorene (18) (ref. 12*a*)	7.96	7.52	7.37	7.37		1.80	2,15, 2.18		2.49, 3.88d (19)	2.91	2.65	1.37
Xanthen (16)	8.31dd (8 and 1)	7.97dd (8 and 1)	7.49m	7.49m	2.21		1.90, 2.00	1.40d (7)	3.08dq (7 and 7)	3.26d (7)	4.80	1.71
With acid [g]	br	br	br	br	br		1.92, 2.05	1.46d (7)	br	3.32d (7)		1.73
Xanthen (20) (ref. 12*b*)	8.10	7.97	7.70	7.45	2.33		2.01, 2.06		2.54 3.20d (19)		4.75	1.30, 1.54
With acid [g]	br	br	br	br	br		2.01, 2.06		br		4.75	1.30, 1.54

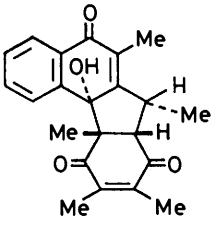
[a] Saturated solutions in $CDCl_3$; first-order coupling constants (Hz) are shown in parentheses, and multiplicities are designated thus: d, doublet; m, unanalysed multiplet. [b] Acid solutions were obtained by adding 2—3 drops of trifluoroacetic acid to the neutral solution. Marked band-broadening is noted by br; in every case sharpness was restored by addition of D_2O or pyridine. [c] All bands were quartets, *J ca.* 1 Hz. [d] Removed by D_2O. [e] Immediately after addition. [f] 1.5 h after addition. [g] No change with time during 3 h.

In order to explain a resonance at δ 0.92 it is therefore necessary to find a geometry in which there are shielding and deshielding effects that can sum to zero. Models show that there is one, and only one, suitable geometry. The ring fusion produced by the addition reaction must given later suggest for the secondary methyl group the configuration shown in (13), *i.e.* methyl *cis* to the hydroxy-group. The n.m.r. spectrum tends to confirm this orientation, for the methine proton resonates as a quintet (double quartet) at δ 3.58. Such a low-field

signal points to major deshielding and again models show that the carbonyl group at position 8 is responsible; the proton on C-7 lies close to the centre of the carbonyl group and almost exactly in its plane so that the predicted downfield shift would be at least 0.6 p.p.m.

An isomeric fluorene alcohol was also isolated. It was very like the first, but with differences in the n.m.r. spectrum suggesting that it might be the epimer at position 7a, *i.e.* the *cis*-fused analogue with structure (14). In particular, the angular methyl group would once more be deshielded by the whole array of unsaturated groupings and resonate at low field (in fact, at δ 1.62), while the torsion angle between the methine protons would diminish (J 7 Hz is observed) and one of them would no longer be selectively deshielded by the nearby carbonyl group (the observed shift at δ 2.75 has moved upfield by *ca.* 0.8 p.p.m.). Epimerisation would relieve the strain of *trans*-fusion and could be induced by the reaction conditions (sodium acetate in methanol); unfortunately, when re-submitted to these conditions, the first isomer (13) gave a mixture of products including trimethylbenzoquinone, which shows that the addition is reversible and thus invalidates any conclusion.

In another effort to achieve epimerisation, the first isomer (13) in trichloromethane was treated with trifluoroacetic acid and the reaction monitored by n.m.r. spectroscopy. There was an immediate change in which several bands moved downfield. Chiefly affected were those from the enone methyl group and some of the aromatic protons; less affected were those from the two methine protons and the angular methyl group, and the rest were hardly altered (Table 1). In the course of an hour or two there was a slow change which restored the original spectrum almost exactly. The second fluorene



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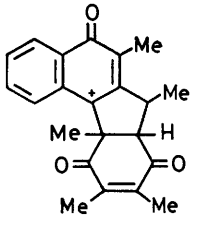
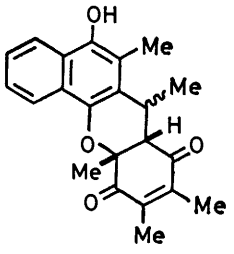


(15)

alcohol (14) behaved in almost exactly the same way except that the shift induced for the enone methyl band was smaller (Table 1). Each isomer retained its identity and no interconversion occurred. The changes are hardly large enough to correspond to the formation of the carbonium ion (15), but they might be due to the protonation of hydroxy-groups;[9] then the return to the original spectrum could be understood as the formation *via* carbonium ion (15) of the corresponding trifluoroacetates (13 or 14; $OCOCF_3$ for OH). Carbonium ion rearrangements would not be expected, since none of them leads to a carbonium ion with stabilisation better than the original benzylic conjugation. Nor would inversion be expected at the carbonium centre; it relieves no strain, and the nucleophile enters from the less hindered side to regenerate the original stereochemistry. The alcohol (13) was recovered from its solution in concentrated hydrochloric acid in methanol. Since the isomers retain their identities the argument precludes the alcohol centre as the point of difference between them; it is also important that line broadening is not noticeable, for this confirms the absence of xanthen (6-hydroxychroman) nuclei in both alcohols.[10]

A third product from the carbanion reaction did suffer extensive broadening of some of its n.m.r. lines (Table 1) and could therefore be recognised as a derivative of 6-hydroxychroman, *i.e.* the xanthen derivative (16). The i.r. spectrum included a broad, complex band with maxima at 1 675 and 1 685 cm^{-1} confirming the presence of the ene-dione grouping and the absence of any further carbonyl groups. The orientation shown in (16) was



(16)

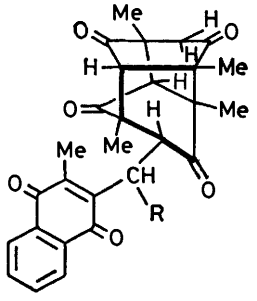
selected because the n.m.r. spectrum showed an ABX_3 spin system, confirmed by spin-decoupling (Table 1). The orientation of addition is therefore the same as that noted previously for xanthen formation, but we have no compelling evidence for the *cis* ring fusion. Generally a *cis*-fusion would be expected for either the [4 + 2] cycloaddition or for a stepwise sequence, but it might be modified by epimerisation; however, the dull orange-brown colour of the compound is unlike that of simple quinones or ene-diones and, as in a previous example, is understood to be a charge-transfer band arising from a transition between the ene-dione (acceptor) and naphthol (donor) in the *cis*-relation.

The xanthen was more easily obtained by generating the carbanion with dilute sodium hydroxide. The liberation of nitrogen was much faster than with the weaker base and the reaction time greatly shortened. The main product under these conditions is the xanthen; a little of the *trans*-alcohol (13) was also produced, but the isomer (14) was not detected.

The last reaction of the carbanion (2b) to be examined in detail was its addition to 2,5-dimethyl-1,4-benzoquinone (2 mol). The reaction was again very complex, and only one compound was isolated sufficiently pure and in good enough yield (35%) to merit study. The yellow colour and other spectroscopic characteristics all pointed to the presence of a 2-methylnaphthoquinone residue along with a cage structure[11] as in (17a). Thus the major carbonyl absorption was above 1 720 cm^{-1}, and five methyl resonances were at high fields consistent only with attachment to saturated groupings. The

n.m.r. spectrum (Table 2) was insensitive to acid. Two sets of multiplets were seen; in one, one methine proton was coupled to another as well as a methyl group, which established the point at which the carbanion became attached to the first dimethylbenzoquinone residue. The other was a simple AB quartet, which showed where in the second dimethylbenzoquinone residue the Michael additions terminated.

By themselves these facts allow several cage structures. The saturated carbonyl groups absorb at 1 732 and 1 725 cm^{-1}, the highest of these frequencies being at the low end of the range for cyclopentanones, or at the high end of the cyclohexanone range. Whatever the cage structure, it would contain features expected to raise rather than lower carbonyl frequencies (*e.g.* ring strain, resonance interactions, dipole interactions) and in another such study satisfactory structures resulted only when frequencies up to 1 740 cm^{-1} were assigned to cyclohexanone carbonyl groups and, frequencies around 1 760 cm^{-1} to cyclopentanone groups.[11] Hence we consider the present cage compound to have only cyclohexanone rings, from which structure (17a) follows uniquely. Table 2 shows the very close correspondence in n.m.r. signals between this compound and one (17b) already reported briefly.[11]



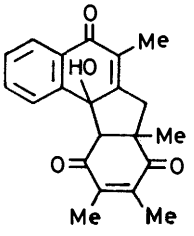
(17)

a, R = Me

b, R = H

It is now clear that the ethyl carbanion (3b) does behave somewhat differently from the methyl carbanions studied previously, the most important difference being the inverted regiospecificity that leads to the fluorene alcohol (13) instead of one analogous to (12). The change-over might be a way of avoiding the bunching of three methyl groups evident in (11a), the poor yield (<20%) being understandable on the same grounds. The indications that the fluorene alcohol (13) is *trans*-fused are in agreement with the requirements of orbital symmetry, which could not be tested before because the fluorene alcohols [*e.g.* (18)] then available were unsuitable.[1] An n.m.r. spectrum of (18) [12a] could not be obtained originally and is now included in Table 1 for comparative purposes; because its angular methyl group is in the wrong angle the test for fusion geometry fails and we still cannot demonstrate *trans*-fusion for this molecule. However, models show that a transition state for *trans*-addition is easily reached; the interacting π systems can act in perpendicular planes as in keten [2 + 2] additions, provided that the carbanion methyl group is kept out of the way as in configuration (19). Of course there is now steric interaction between the two methyl groups, but this can be relieved by a moderate out-of-plane twisting, which has an important advantage in that it causes the anionic π orbital to improve its overlap with the incoming quinone π orbitals. These considerations lead to the configuration assigned in (13) to the secondary methyl group.

The n.m.r. spectrum of the xanthen derivative (20) [12b] is also included in Table 1. No special feature emerges, largely because the *cis*-fused molecules are very flexible. We have no clear grounds for assigning a configuration to the secondary methyl group in structure (16).



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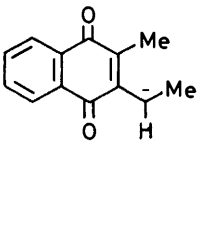
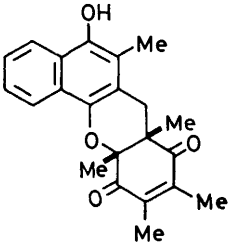


(19)



(20)

Thus we have not observed a condensation like that in (4). It may be that, in addition to the carbanionic methyl group, a vacant 3-position is required; our method of generating carbanions is unsuited for such situations. Since the conditions used to produce (2) were very vigorous, it might also be that all the condens-

TABLE 2

^{1}H N.m.r. spectra * of cage ketones (17a) and (17b)

	Ar-H (*ortho* to C=O)	Ar-H (other)	C*H*CHMe	CHC*H*Me	ring-CH_2		ring-CH		quinone Me	bridge CH*Me*	Me	Me	Me	Me
(17a)	8.08m	7.65m	4.02d (9)	3.05m	2.90d (19)	2.48d (19)	2.55s	2.33s	2.02s	1.46d (7)	1.30s	1.22s	1.12s	1.01s
					−CH−CH_2									
(17b)	8.03 (m)	7.65 (m)	3.68, 2.76, 2.71 (J_{AX} 7; J_{BX} 9)		2.92 (d, 19)	2.46 (d, 19)	2.49 (s)	2.41 (s)	2.14s		1.26s	1.17s	1.14s	1.08s

* Compound (17a) at 220 MHz, compound (17b) at 100 MHz; both in $CDCl_3$ with tetramethylsilane as internal standard. Relative intensities are those required by the assignments. Coupling constants (Hz) are given in parentheses.

ations we observe are reversible and that (2) represents a thermodynamically controlled destination.

EXPERIMENTAL

U.v. spectra were determined on *ca.* 10^{-3}M solutions in ethanol. Molecular weights were determined mass spectroscopically. Samples for elementary analysis were dried at 110 °C at 20 mmHg for 4 h.

3,3a-*Dihydro*-3a-*methylbenz*[f]*indazole*-4,9(2H)-*dione* (7).—Diazomethane was allowed to react with 2-methyl-1,4-naphthoquinone as described previously.[5] The solid was filtered off and air blown through the mother-liquor to remove solvent and any excess of diazomethane. The remaining bright yellow oil was chromatographed on neutral alumina (Grade III) eluting with trichloromethane; a slow-moving yellow band was eluted separately and its contents crystallised from trichloromethane–light petroleum (b.p. 60—80 °C) to give the *indazoledione* as yellow pointed prisms, m.p. 175—176 °C; $\lambda_{max.}$ 239, 260infl., 306, and 342 nm (log ε 4.18, 3.88, 3.60, and 3.70); $\nu_{max.}$ (mull) 3 220 (NH), 1 697, 1 638, and 1 590 cm^{-1}; δ ($CDCl_3$) 8.32 and 8.10 (each 1 H, d, Ar-H *ortho* to C=O), 7.82 (2 H; other Ar-H), 3.83 and 4.12 (each 1 H, d, *J* 12 Hz, ring-CH_2), 1.46 (3 H, s, Me), and 1.28 (1 H, br, NH) (Found: 67.5; H, 4.9; N, 10.2%; *M*, 214. $C_{12}H_{10}N_2O_2$ requires C, 67.3: H, 4.7; N, 13.1%; *M*, 214).

2-*Ethyl*-3-*methyl*-1,4-*naphthoquinone*.—A mixture of the epimers (5a) (0.19 g) in acetonitrile (10 ml, dried over molecular sieves) was treated with triethylamine (0.10 g) and kept at 18 °C for 25 h. The solution was diluted with ether (100 ml) and most of the acetonitrile and base removed by copious washing with water; the solution was then dried ($MgSO_4$) and concentrated *in vacuo*, and the product purified from benzene on a column of silica. The only crystalline fraction gave the quinone, which separated from light petroleum in clusters of small, yellow needles (0.05 g), m.p. 72 °C (lit.,[8] 72 °C), further identified spectroscopically.

But-2,3-*ylidene*-2,2′-*bis*-(3-*methyl*-1,4-*naphthoquinone*) (9).—A mixture of the epimers (5a) (0.19 g) in chloroform (2 ml) and methanol (10 ml) was treated with three drops of 2M-sodium hydroxide. Nitrogen was evolved at once and the solution became blue for a short time, and then dark red. Yellow crystals slowly separated and were collected after 1 h; a further crop was obtained by concentration of the mother-liquors and chromatography on silica. The combined solids were recrystallised from methanol containing a little chloroform to give the *butylidenediquinone* as yellow prisms (0.13 g), m.p. 252—253 °C; $\lambda_{max.}$ 248, 258, 270, and 330 nm (log ε 4.57, 4.33, 4.30, and 3.75); $\nu_{max.}$ (mull) 1 660, 1 610, 1 593 (naphthoquinone triad), and 723 cm^{-1}; δ 1.19 (6 H, d, *J* 7 Hz, CH*Me*), 2.41 (6 H, s, quinone Me), 3.96 (2 H, m, C*H*Me), *ca.* 8.1 (2 H, m, Ar-H *ortho* to CO), and *ca.* 7.70 (2 H, m, other Ar-H) (Found: C, 78.2; H, 5.6. $C_{26}H_{22}O_4$ requires C, 78.4; H, 5.6%).

7,7a-*Dihydro*-6,7,7a-*trimethyldibenzo*[b,j]*fluorene*-5,8,13-*trione* (11a).—A mixture of the epimers (5a) (0.57 g) and 2-methyl-1,4-naphthoquinone (0.90 g) in methanol (30 ml) containing trichloromethane (3 ml) was treated with sodium acetate trihydrate (0.71 g) in methanol (10 ml) at 22 °C. After 35 min, the yellow precipitate was collected, washed with methanol, and crystallised from dioxan to give the *trione* as yellow plates (0.12 g), m.p. 232—234 °C; $\lambda_{max.}$ 236, 262, 288, 333, 350, and 393 nm (log ε 4.16, 3.90, 3.90, 3.92, 3.92, and 4.08); $\nu_{max.}$ (KBr) 1 692, 1 625, and 1 592 cm^{-1}; δ ($CDCl_3$, 100 MHz) 8.98 (1 H, dd, *J* 8 and 2 Hz, H-1), 8.35 (3 H, m, Ar-H *ortho* to CO), 7.87 (2 H, m) and 7.64 (2 H, m) (other Ar-H), 3.50 (1 H, q, *J* 7 Hz, C*H*Me), 2.30 (3 H, s, vinylic Me), 1.57 (3 H, s, angular Me), and 1.28 (3 H, d, *J* 7 Hz; CH*Me*) (Found: C, 81.3; H, 5.1. $C_{24}H_{18}O_3$ requires C, 81.3; H, 5.1%). An additional crop (0.15) was secured from the mother-liquors by removing the solvents and chromatographing the residue on silica; benzene–light petroleum (1 : 1) removed unreacted quinone, then benzene alone eluted the desired material. No other fractions gave workable amounts of crystalline products.

6-*Benzyl*-7,7a-*dihydro*-7,7a-*dimethyldibenzo*[b,j]*fluorene*-5,8,13-*trione* (11b).—As in the foregoing case, ethereal diazoethane from nitrosoethylurea (16 g) was mixed with 2-benzyl-1,4-naphthoquinone (2.2 g) in ether (150 ml) at 0 °C. After 1 h the solution was concentrated (*in vacuo* without external heating) to *ca.* 50 ml. The product slowly separated and when purified by rapid crystallisation from ether–light petroleum (1 : 1) supplied 9a-*benzyl*-3a,9a-*dihydro*-3-*methylbenz*[f]*indazole*-4,9(3H)-*dione* (5b) as needles (1.9 g), m.p. 102—103 °C (decomp.); $\nu_{max.}$ (mull) 1 678, 1 592, and 1 554 cm^{-1}; δ ($CDCl_3$, 100 MHz) 7.94 (2 H, mm, Ar-H *ortho* to CO), 7.28 (2 H, m, other Ar-H), 4.43 (1 H, m, C*H*Me), 3.95 and 3.60 (each 1 H, d, benzylic AB system), 2.70 (1 H, d, *J* 9 Hz; CHC*H*CO), and 1.35 (3 H, d, *J* 7 Hz; CH*Me*) (Found: C, 74.9; H, 5.2; N, 8.9. $C_{19}H_{16}N_2O_2$ requires C, 74.9; H, 5.3; N, 9.2%). This compound in methanol liberated nitrogen when treated with dilute aqueous sodium hydroxide, but the organic products were tarry.

This indazole (0.78 g) and 2-methyl-1,4-naphthoquinone (0.86 g) were dissolved in methanol (30 ml) containing trichloromethane (5 ml), and treated with sodium acetate trihydrate (0.6 g) in methanol (10 ml). Nitrogen was evolved and the deep orange solution slowly deposited a yellow solid. This was collected after *ca.* 1 h and a further quantity obtained from the mother-liquors by concentrating them and chromatographing the product on silica, first by means of benzene–light petroleum (to remove the rest of the quinone) and then by means of neat benzene, which eluted the desired material. The combined solids were purified from methanol containing a little trichloromethane to give the *fluorenetrione* as deep yellow plates (0.29 g), m.p. 212—213 °C; $\lambda_{max.}$ 239, 287, 333, 348, and 384 nm (log ε 4.45, 3.98, 3.97, 3.97, and 3.94), $\nu_{max.}$ (KBr) 1 695, 1 653, 1 635, 1 623, and 1 600 cm^{-1}; δ ($CDCl_3$, 100 MHz) 8.61 (1 H, dd, *J* 8 and 2 Hz, H-1), 8.16 (3 H, m, Ar-H *ortho* to CO), 7.71 (2 H, m) and 7.49 (2 H, m) (other naphthoquinone Ar-H), 7.13 (5 H, benzyl Ar-H), 4.08 and 3.73 (each 1 H, d, *J* 15 Hz, benzylic AB system), 3.43 (1 H, q, *J* 7 Hz, C*H*Me), 1.25 (3 H, s, angular Me), and 1.14 (3 H, d, *J* 7 Hz; CH*Me*) (Found: C, 83.5; H, 5.4. $C_{30}H_{22}O_3$ requires C, 83.6; H, 5.2%).

Reactions with Trimethyl-1,4-*benzoquinone*.—Sodium acetate trihydrate (1.6 g) in methanol (15 ml) was stirred into a mixture of the indazole epimers (5a) (1.3 g) in trichloromethane (5 ml) and trimethylbenzoquinone (1.8 g) in methanol (40 ml). The mixture became dark red while nitrogen was evolved and then the colour faded to yellow. After 35 min the mixture was diluted with water (30 ml) and acidified with 2M-hydrochloric acid. The organic products were extracted into dichloromethane (3 × 50 ml), washed with water, dried (Na_2SO_4), and recovered by evaporation under reduced pressure to a thick red oil. This was dissolved in a small amount of trichloromethane, and light petroleum (b.p. 40—60 °C) was added to initiate crystallisation. When no more solid separated the mother-

liquors were removed by decantation and the residue dissolved in benzene and left overnight; it deposited a colourless solid that, after further purification from benzene, supplied (7R*, 7aR*, 11aS*, 11bS*)-7,7a,11a,11b-*tetrahydro*-11b-*hydroxy*-6,7,9,10,11a-*pentamethylbenzo*[c]*fluorene*-5,8,11-*trione* (13) as *plates* (0.21 g), m.p. 213—215 °C; $\lambda_{max.}$ 251 and 282 nm (log ε 4.20 and 3.78); $\nu_{max.}$ (KBr) 3 390 (OH), 1 665 (broad complex band, ene-dione C=O), 1 665 (broad, acrylophenone C=O), 1 640 and 1 595 (ene and aromatic), and 770 and 720 cm^{-1} (aromatic) (Found: C, 75.2; H, 6.4%; *M*, 350. $C_{22}H_{22}O_4$ requires C, 75.4; H, 6.3%; *M*, 350).

The decanted mother-liquor was freed from solvent under reduced pressure at 20 °C and the residue was dissolved in ether and set aside. An orange solid separated and was purified from ethanol to give 7a,11a-*dihydro*-5-*hydroxy*-6,7,9,10,11a-*pentamethylbenzo*[c]*xanthen*-8,11(7H)-*dione* (16) as orange needles (0.25 g), m.p. 191—193 °C; $\lambda_{max.}$ 243, 310, 320, and 334 nm (log ε 4.89, 3.99, 4.03, and 3.94); $\nu_{max.}$ (KBr) 3 470 (OH), 1 688 and 1 672 (ene-dione C=O), 1 610 and 1 598 (ene and aromatic), and 763 cm^{-1} (aromatic) (Found: C, 75.1; H, 6.4%; *M*, 350. $C_{22}H_{22}O_4$ requires C, 75.4; H, 6.3%; *M*, 350).

All the mother-liquors remaining after the foregoing operations were combined and the solvents removed *in vacuo* to give a syrup that was chromatographed (trichloromethane eluant) on a column of neutral alumina (Grade III). The first fractions to separate were clear yellow and contained trimethylbenzoquinone. The next fractions were faintly yellow and supplied a product that, purified from benzene, gave (7R*, 7aS*, 11aS*, 11bS*)-7,7a,11a,11b-*tetrahydro*-11b-*hydroxy*-6,7,9,10,11a-*pentamethylbenzo*[c]*fluorene*-5,6,11(7H)-*trione* (14) as faintly yellow rods (0.16 g), m.p. 241—242 °C; $\lambda_{max.}$ 249, 289, 312, 322, and 330 nm (log ε 5.10, 4.00, 3.60, 3.48, and 3.30); $\nu_{max.}$ (KBr) 3 440 (OH), 1 675 and 1 658 (complex band, ene-dione (C=O), 1 640 (complex, acrylophenone C=O), 1 610 and 1 595 (ene and aromatic), and 710 cm^{-1} (aromatic) (Found: C, 74.6; H, 6.4%; *M*, 350. $C_{22}H_{22}O_4$ 0.25 H_2O requires C, 74.5; H, 6.4%; *M*, 350).

These fractions were found by n.m.r. spectroscopy to contain further quantities of the fluorene alcohol (14) along with a closely similar substance that may be another epimer. The two substances could not be separated. Several other fractions were obtained by chromatography but none contained workable amounts of crystalline material.

Xanthone (16); *Alternative Preparation*.—The mixture of epimers (5a) (0.65 g) was dissolved in methanol (20 ml) containing trimethylbenzoquinone (1.0 g) and 0.1 M-sodium hydroxide (0.2 ml) was added at 22 °C. The yellow solution rapidly became dark orange and nitrogen was evolved briskly; when this ceased (up to 4 min) the solution was diluted with water, acidified with 2M-hydrochloric acid, and extracted with dichloromethane. The products formed a dark syrup that was dissolved in the minimum volume of trichloromethane and treated with light petroleum (b.p. 60—80 °C) to precipitate a solid. This solid first dissolved in ethanol and then deposited the fluorene alcohol (13) (50 mg), m.p. 214—215 °C. The mother-liquor was concentrated *in vacuo* at room temperature and the residue crystallised from benzene to give the xanthen (16) as an orange solid (300 mg), m.p. 190—192 °C. A further quantity (106 mg) of the xanthen was obtained by concentrating the filtrate and cooling it.

Reactions of the Fluorene Alcohol (13).—(i) *With sodium acetate*. The fluorene alcohol (30 mg) was suspended in methanol (5 ml) and treated with sodium acetate trihydrate (0.2 g) with stirring. The mixture became yellow and after 45 min the fluorene alcohol had dissolved completely. After 2 h the solution was diluted with water (15 ml), acidified with 2M-hydrochloric acid, and extracted with dichloromethane. Chromatography indicated the presence of four compounds and n.m.r. spectroscopy identified one of them as trimethylbenzoquinone. The others were not identified but none had the characteristics of the isomeric fluorene alcohol (14). This result was not much altered by quenching the reaction after only 45 min.

(ii) *With hydrochloric acid*. The fluorene alcohol (30 mg) suspended in methanol (5 ml) was stirred with concentrated hydrochloric acid (1 ml) at 20 °C for 2 h. The product was isolated by means of dichloromethane and formed a solid that, crystallised from ether, supplied the original alcohol (identified by chromatography and n.m.r. spectroscopy) as prisms (27 mg).

1,2,3,4,4a,5,6,7,8,8a-*Decahydro*-1,4,4a,7-*tetramethyl*-6-[1-(3-*methyl*-1,4-*naphthoquinon*-2-*yl*)]*ethyl*-1,4,7-(1-*ethanyl*-2-*ylidene*)*naphthalene*-1′,3,5,8-*tetraone* (17a.)—To a mixture (0.54 g) of the indazole epimers (5a) in trichloromethane (5 ml) was added first 2,5-dimethyl-1,4-benzoquinone (1.0 g) in methanol (40 ml) and then sodium acetate trihydrate (0.7 g) also in methanol (40 ml). During 2 h at room temperature a yellow solid separated, which was collected and washed with methanol, and then crystallised from ethanol to give the *tetraone* as tiny yellow crystals (0.35 g), m.p. 242—243 °C; $\lambda_{max.}$ 247, 266, and 326 nm (log ε 4.24, 4.14, and 3.59); $\nu_{max.}$ (KBr) 1 732 with a major sub-maximum at 1 725 and shoulders at 1 742 and 1 720 (cycloalkane carbonyl groups), 1 650, 1 610, and 1 590 (naphthoquinone pattern), and 720 cm^{-1} (Found: C, 73.3; H, 5.8%; *M*, 472. $C_{29}H_{28}O_6$ requires C, 73.6; H, 5.9%; *M*, 472). The ^1H n.m.r. spectrum is in Table 2. T.l.c. of the residue from the tetraone showed several constituents, none in large enough amounts to make further study attractive.

[9/1647 *Received*, 17*th October*, 1979]

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