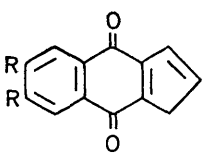
Synthetic Routes to Benz[*f*]indenes

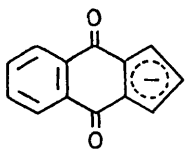
By **Robin G. F. Giles** * and **Ivan R. Green**, Department of Chemistry, University of Cape Town, South Africa

An attempt to make benz[*f*]indene-4,9-quinone (I; R = H) by a reverse Diels–Alder route was unsuccessful because of the instability of this compound. A similar reaction to give the corresponding quinol dimethyl ether (III; R^1 = H, R^2 = Me) proved to be very efficient. The related 6,7-dimethylbenz[*f*]indene-4,9-diyl diacetate (III; R^1 = Me, R^2 = Ac) was synthesised by bromination–dehydrobromination of 2,3-dihydro-6,7-dimethylbenz-[*f*]indene-4,9-diyl diacetate.

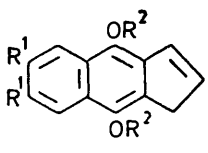
THE considerable stability possessed by cyclopentadienide ions has been ascribed to their having $(4n + 2)$ π-electrons.[1] We record here an investigation of routes to the quinone (I; R = H), from which the Hückel aromatic anion (II), isoelectronic with anthraquinone might be derived. Although the quinone itself has not yet been isolated because of its apparent instability, the dimethyl ether (III; R^1 = H, R^2 = Me) of the corresponding quinol has been obtained in high yield.



(I)



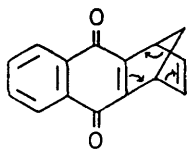
(II)



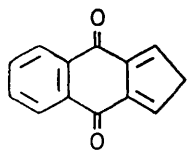
(III)

Removal of the ethylenic bridge from the quinone (IV) by a retro-Diels–Alder reaction as indicated might be anticipated to give rise to the diacyl cyclopentadiene (V), a tautomer of (1). A related transformation of bicyclo[2.2.1]heptadiene to cyclopentadiene has recently been reported, in which either the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (VI)[2] or 3,6-di-(2-pyridyl)-*s*-tetrazine (VII)[3] was used as acetylene scavenger.

The quinone (IV) did not react appreciably with the enophiles (VI), (VII), or tetraphenylcyclopentadienone. However, the more reactive dienone phencyclone (VIII) did add to the less hindered *exo*-side of the quinone (IV), to give a compound to which either structure



(IV)



(V)

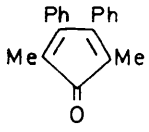
(IXa) or (IXb) may be assigned. The i.r. spectrum showed carbonyl stretching bands at 1793 and 1656 cm^{-1}, attributable to ketone and quinone, respectively. That *exo*-addition had taken place was supported first by the lack of coupling[4] between the bridgehead protons (τ 6·23) and the neighbouring *endo*-protons (τ 6·85) and secondly by the results of a photochemical experiment (see later) in which a product (XIII) of alternative *endo*-addition was shown to undergo cage formation upon irradiation. The adduct (IX) did not behave similarly. Of the two structures (IXa) and (IXb) the former might be preferred by analogy with the structure of the adduct from the dienone (VI) and bicyclo[2.2.1]heptadiene.[2]

Pyrolysis of the adduct (IX) at 230° under nitrogen gave rise to 1,4-diphenyltriphenylene (X) and intractable material. In a repeat experiment, sublimation of the

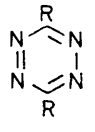
[1] F. R. Goss and C. K. Ingold, *J. Chem. Soc.*, 1928, 1268.
[2] W. S. Wilson and R. N. Warrener, *Tetrahedron Letters*, 1970, 5203.
[3] W. S. Wilson and R. N. Warrener, *J.C.S. Chem. Comm.*, 1972, 211.
[4] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1171.

pyrolysis products onto a cold finger gave, in addition to (X), a yellow substance which darkened rapidly on exposure to air or on further heating. This was too unstable for identification, even by trapping as an adduct (see Experimental section).

Attempts were made to prepare the spirocyclopropane (XI), a derivative of (V) in which the possibility of hydrogen migration could be excluded. The quinone (XII) was obtained by addition of spiro[2,4]hepta-4,6-diene to naphthaquinone, enolisation of the adduct with potassium t-butoxide in dry tetrahydrofuran, and subsequent oxidation of the intermediate quinol with silver oxide. These conditions were used to prevent the ready formation of a mixture of epoxides of the quinone (XII).[5] Phencyclone added to the *endo*-face of the

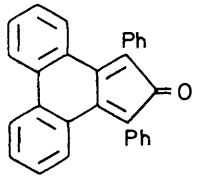


(VI)

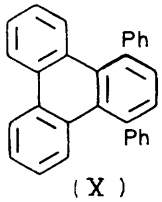


R = 2 – pyridyl

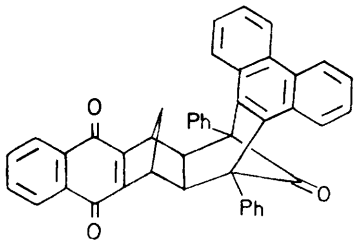
(VII)



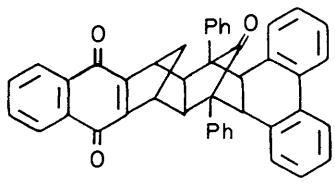
(VIII)



(X)



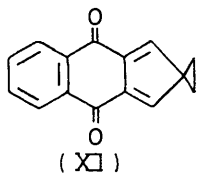
(IXa)



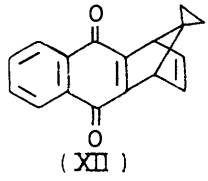
(IXb)

quinone (XII) [*cf.* *exo*-addition to (IV)] to give the adduct (XIII). That the adduct (XIII) had the stereochemistry indicated was shown by the fact that it underwent an internal photocycloaddition in sunlight in the crystalline form to yield the colourless cage compound (XIV), whose i.r. spectrum showed carbonyl absorptions at 1770 and 1680 cm^{-1}. The contrasting *exo*-mode of addition of phencyclone to the quinone (IV) was further demonstrated by the lack of similar photoreactivity in the case of the product (IX). The difference in stereochemistry of the adducts (IX) and (XIII) may be attributed to the *exo*-face of (XII) being more hindered than that of (IV).

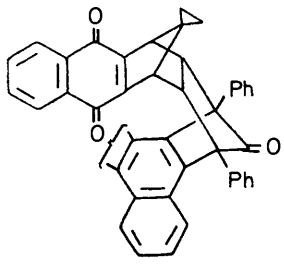
Pyrolysis of adduct (XIII) gave rise to the triphenylene (X) in 70% yield. Once again, extensive darkening of the reaction mixture took place and the desired compound (XI) could be neither isolated nor trapped.



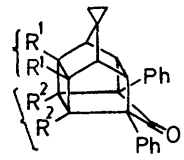
(XI)



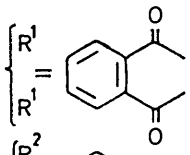
(XII)

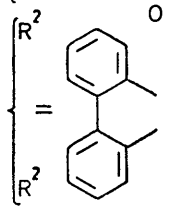


(XIII)

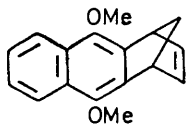


(XIV)

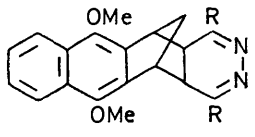




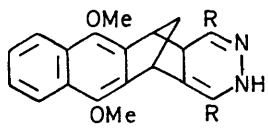
Whereas the quinone (IV) resisted addition to the enophiles (VI) and (VII), the dimethyl ether (XV) of the corresponding quinol added to both. Reaction with the tetrazine proceeded rapidly at room temperature.* Nitrogen evolution yielding the desired compound (XVI) was followed by hydrogen migration to give the 1,4-dihydropyridazine (XVII) quantitatively, as evidenced by a low field NH n.m.r. singlet at τ 0·60 (removed by D_2O) and by an i.r. absorption at 3360 cm^{-1}.



(XV)



(XVI)



(XVII)

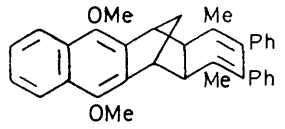
R = 2 – pyridyl

As the intermediate (XVI) required for the reverse Diels–Alder reaction could not be isolated, an alternative

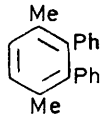
* We thank Mr. G. H. P. Roos for performing this experiment.

[5] R. G. F. Giles and I. R. Green, *J.C.S. Chem. Comm.*, 1972, 1332.

route to (III; $R^1 = H$, $R^2 = Me$) was sought. Compound (XV), on prolonged heating under reflux with the dienone (VI) in chlorobenzene, gave the diene (XVIII) in



(XVIII)

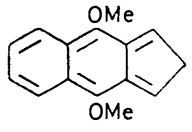


(XIX)

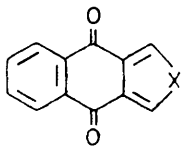
high yield. That the initially formed bridged ketone had undergone elimination of carbon monoxide to form the diene (XVIII) was evidenced by the lack of carbonyl i.r. absorption and by the position of the *C*-methyls n.m.r. signals at τ 8·28, which indicated attachment to olefinic carbon atoms. Furthermore, lack of coupling between the bridgehead and the neighbouring methine protons supported the *exo*-structure.

Pyrolysis of (XVIII) at 305° for *ca.* 2 min, followed by sublimation of the pyrolysate, afforded the dimethyl ether (III; $R^1 = H$, $R^2 = Me$) in 90% yield, together with 3′,6′-dimethyl-*o*-terphenyl (XIX). In addition to aromatic and methoxy-signals, the n.m.r. spectrum of (III; $R^1 = H$, $R^2 = Me$) showed signals attributable to two olefinic protons, each as doublets further split into triplets centred at τ 2·86 (J 2 and 5·8 Hz) and 3·4 (J 2 and 5·8 Hz) and the methylene protons at τ 6·40 (J 2 Hz). Formation of (III; $R^1 = H$, $R^2 = Me$) may be rationalised in terms of the intermediacy of the 2*H*-benzindene (XX). Attempts to oxidise the indene (III; $R^1 = H$, $R^2 = Me$) to the quinone (I; R = H) have so far proved fruitless.

The considerable difference in stability between the quinone methides (V) and (XI), and the related heterocyclic systems (XXI) [6] is worthy of note.



(XX)



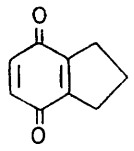
(XXI)

X = S, NR or O

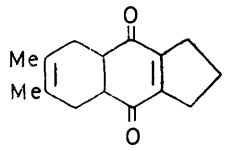
In view of the lack of success in obtaining the quinone (I; R = H), an alternative route to compounds of this type was sought. Reaction between 2,3-dimethylbuta-1,3-diene and indane-4,7-quinone (XXII) [7] readily afforded the adduct (XXIII), which was aromatised to the quinone (XXIV; R = H) in high yield by base-catalysed enolisation to the quinol (XXV), and subsequent treatment first with nitrous acid in glacial acetic acid and then with sodium dichromate. Oxidation of (XXV) with silver oxide afforded the quinone (XXVI).

Introduction of a double bond into the five-membered ring of (XXIV; R = H) would formally give the quinone (I; R = Me). This was attempted by bromination–dehydrobromination. Bromination with 1 equiv. of *N*-bromosuccinimide gave an unstable product whose ^1H n.m.r. spectrum indicated it to be the monobromo-compound (XXIV; R = Br). Attempted dehydrobromination with a variety of bases led to extensive decomposition and neither the quinone (I; R = Me) nor the anion derived therefrom was observed.

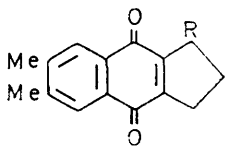
Reductive acetylation of the quinone (XXIV; R = H) afforded the diacetate (XXVII; R = H), which was in turn monobrominated with *N*-bromosuccinimide.



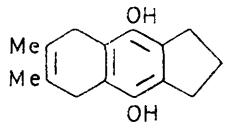
(XXII)



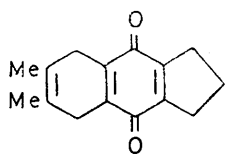
(XXIII)



(XXIV)



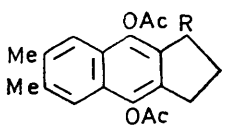
(XXV)



(XXVI)

Treatment of the product (XXVII; R = Br) with lutidine afforded the diacetate (III; $R^1 = Me$, $R^2 = Ac$) in 60% yield.

Hydrolysis of this indene diacetate with aqueous potassium hydroxide gave a black precipitate from which the quinone (XXIV; R = H) was isolated in 15% yield as the sole product. Its formation may be rationalised in terms of the intermediacy either of the quinol (III; $R^1 = Me$, $R^2 = H$), with which the quinone (XXIV; R = H) is tautomeric, or of a related anion which could similarly be converted into the observed product.



(XXVII)

EXPERIMENTAL

Unless otherwise stated i.r. spectra were measured for Nujol mulls and n.m.r. spectra for solutions in [^{2}H]chloroform with tetramethylsilane as internal reference. Chromatography was carried out using Merck Kieselgel (30—70 mesh).

1,4-*Dihydro*-1,4-*methanoanthraquinone* (IV).—(a) 1,4-*Di*-

[6] D. W. H. MacDowell, R. A. Jourdenais, R. W. Naylor, and J. C. Wisowaty, *J. Org. Chem.*, 1972, **37**, 4406, and references quoted therein.

[7] H. J. Teuber and W. Rau, *Chem. Ber.*, 1953, **86**, 1036.

hydro-1,4-*methanoanthraquinol*. The naphthoquinone–cyclopentadiene adduct[8] (6·1 g) in dry tetrahydrofuran (250 ml) was flushed with nitrogen. Potassium t-butoxide (0·6 g) was added and the resulting solution was stirred for 30 min, neutralised with dilute hydrochloric acid, poured into water, and extracted with chloroform; the extract was dried ($MgSO_4$), and evaporated to give the *quinol* (6·1 g), m.p. 168° (decomp.) (from chloroform–petroleum) (Found: C, 80·4; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·0; H, 5·4%), $\lambda_{max.}$ 252, 280, 310, 327, and 340 nm (log ε 4·40, 3·57, 3·62, 3·63, and 3·58), $\nu_{max.}$ 3280, 1645, and 1605 cm^{-1}, τ [$(CD_3)_2CO$] 2·00 (2H, m, ArH), 2·35 (2H, s, OH, D_2O-exchangeable), 2·70 (2H, m, ArH), 3·37 (2H, t, *J* 1·6 Hz, CH=CH), 5·68 (2H, t, *J* 1·6 Hz, bridgehead H), and 7·93 (2H, m, CH_2).

(b) *The quinone* (IV). The quinol (6·0 g) in benzene (350 ml) was treated with an excess of powdered silver oxide; the mixture was shaken for 5 h and filtered. The filtrate was evaporated to yield the quinone (IV) (100%), m.p. 157° (lit.,[8] 158°), $\lambda_{max.}$ 248, 254, 277, and 339 nm (log ε 4·24, 4·29, 4·20, and 3·46), $\nu_{max.}$ 1660, 1640, and 1600 cm^{-1}, τ 2·11 (2H, m, ArH), 2·49 (2H, m, ArH), 3·22 (2H, t, *J* 2 Hz, CH=CH), 5·83 (2H, m, bridgehead H), and 7·69 (2H, m, CH_2).

1,4-*Dihydro*-1,4-*methanoanthraquinol Dimethyl Ether* (XV). —(a) *From* 1,4-*dihydro*-1,4-*methanoanthraquinol*. A solution of the quinol (4·5 g) in ethanol (60 ml) was heated to 50° and stirred rapidly while 10M-sodium hydroxide (5 ml) and dimethyl sulphate (6 ml) were added alternately during 5 min. Thereafter more sodium hydroxide (2 ml) was added and the resulting solution was heated on a water-bath for 2·5 h. The solvent was evaporated off and the residue partitioned between water (250 ml) and chloroform (5 × 50 ml). The chloroform extract was dried ($MgSO_4$) and evaporated and the residue chromatographed (benzene) to give the *ether* (XV) (93%), m.p. 77° (from methanol) (Found: C, 80·8; H, 6·3. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·4%), $\lambda_{max.}$ 242 and 281 nm (log ε 4·57 and 3·77), $\nu_{max.}$ 1645, 1605, and 1080 cm^{-1}, τ 2·03 (2H, m, ArH), 2·62 (2H, m, ArH), 3·30 (2H, t, *J* 2 Hz, CH=CH), 5·73 (2H, m, bridgehead H), 6·07 (6H, s, OCH_3), and 7·79 (2H, m, CH_2).

(b) *From the naphthoquinone–cyclopentadiene adduct*. The adduct (33·2 g) in ethanol (500 ml) was stirred at 50° under nitrogen while sodium hydroxide (40 g) in water (125 ml) and dimethyl sulphate (80 ml) were added alternately in small quantities. The solution was then gently boiled for 8 h, cooled, and acidified, and the solvent volume was reduced to give the dimethyl ether (36·5 g), m.p. 77° (from methanol), identical with material obtained in (a).

The Phencyclone Adduct (IX).—A solution of (IV) (0·25 g) and phencyclone[9] (1,3-diphenylcyclopenta[*l*]phenanthren-2-one) (0·51 g) was heated under reflux in toluene (40 ml) for 50 h. Unchanged phencyclone was filtered from the cool solution and the filtrate was reduced in volume to 5 ml and diluted with ethanol. The yellow *precipitate* of (IX) was filtered off; m.p. 223—225° (decomp.) (Found: C, 87·3; H, 4·5. $C_{44}H_{28}O_3$ requires C, 87·6; H, 4·6%), $\nu_{max.}$ 1793, 1656, and 1598 cm^{-1}, τ ($CDCl_3$; 50°) 2·0—3·0 (22H, m, ArH), 6·23 (2H, s, bridgehead CH), 6·85 (2H, s, *endo*-CH), and 8·37 (2H, m, CH_2).

Pyrolysis of the Adduct (IX).—Sublimation of the adduct at 230° and 0·5 mmHg under nitrogen formed a mixture ($\nu_{max.}$ 1670 cm^{-1}) which darkened on being heated or on exposure to air. Chromatography of the mixture with chloroform afforded 1,4-diphenyltriphenylene (X), m.p. 221—222° (lit.,[10] 223°) (from methanol–benzene).

In separate experiments, the cold fingers bearing the sublimates from the pyrolyses were dipped into ethereal solutions of potential trapping agents such as *N*-phenylmaleimide, cyclopentadiene, tetracyanoethylene, and the *s*-tetrazine (VII). In no case was any addition product observed.

Diels–Alder Reaction between Naphthoquinone and Spiro-[2,4]*hepta*-4,6-*diene*.—A solution of naphthoquinone (10 g) and the spiro-diene (8·2 g) was heated under reflux in benzene (60 ml) for 12 h. Removal of the solvent and the excess of diene gave 1,4,4a,9a-*tetrahydro*-1,4-*methanoanthracene*-11-*spirocyclopropane*-9,10-*quinone*, quantitatively, m.p, 159—160° (decomp.) (from ethanol) (Found: C, 81·8; H. 5·6. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%), $\lambda_{max.}$ 225, 250, 301, and 309 nm (log ε 4·24, 3·93, 3·13, and 3·12), $\nu_{max.}$ 1678 and 1589 cm^{-1}, τ 1·99 (2H, m, ArH), 2·30 (2H, m, ArH), 3·96 (2H, t, *J* 2 Hz, CH=CH), 6·38 (2H, m, bridgehead CH), 6·98 (2H, m, CH·CO), and 9·42 (4H, m, $CH_2 \cdot CH_2$).

Enolisation and Partial Oxidation of the Naphthoquinone–Spiro-diene Adduct.—The adduct (7·2 g) in dry tetrahydrofuran (150 ml) was stirred at room temperature for 1 h with potassium t-butoxide (1 g) in a flask pre-flushed with nitrogen. The mixture was poured into water, and rapidly neutralised (dilute hydrochloric acid), and extracted with chloroform; the extract was dried ($MgSO_4$) and evaporated. The orange solid was fractionally recrystallised from methanol to yield the quinone (XII), m.p. 186° (0·9 g). Evaporation of the mother liquors yielded 1,4-*dihydro*-1,4-*methanoanthracene*-11-*spirocyclopropane*-9,10-*diol* (6·3 g), m.p. 168—170° (from benzene) (Found: C, 81·4; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%), $\nu_{max.}$ 3260, 1656, 1608, and 1080 cm^{-1}.

The Quinone (XII).—The foregoing quinol (1 g) in benzene (30 ml) containing silver oxide (2·5 g) was shaken for 1 h and the mixture was then filtered. Evaporation gave 1,4-*dihydro*-1,4-*methanoanthracene*-11-*spirocyclopropane*-9,10-*quinone* (100%), m.p. 186° (from ethanol) (Found: C, 82·2; H, 4·7. $C_{17}H_{12}O_2$ requires C, 82·3; H, 4·8%), $\lambda_{max.}$ 248, 254, 278, and 340 nm (log ε 4·23, 4·27, 3·97, and 3·38), $\nu_{max.}$ 1659 and 1598 cm^{-1}, τ 1·92 (2H, m, ArH), 2·32 (2H, m, ArH), 3·05 (2H, t, *J* 2 Hz, CH=CH), 6·27 (2H, t, *J* 2 Hz, bridgehead CH), and 9·37 (4H, m, $CH_2 \cdot CH_2$).

The Phencyclone Adduct (XIII).—The quinone (XII) (1 g) and phencyclone (1·1 g) were heated together under reflux in toluene (100 ml) for 24 h. The solvent (80 ml) was distilled off, and hot ethanol (50 ml) was added to the residue to precipitate on cooling the orange *adduct* (1 g), m.p. 210° (from benzene–methanol) (Found: C, 87·2; H, 4·8. $C_{46}H_{30}O_3$ requires C, 87·5; H, 4·8%), $\nu_{max.}$ 1787, 1663, and 1598 cm^{-1}.

Irradiation of the Adduct (XIII). The adduct (0·5 g) was spread thinly on a watch glass and exposed to sunlight for 6 days with occasional mixing of the crystals in order to expose new surface areas. Reaction was accompanied by a colour change from orange to white. The *photoisomer* (XIV) was thus obtained quantitatively, m.p. >300° (from chloroform–methanol) (Found: C, 87·3; H, 4·5. $C_{46}H_{30}O_3$ requires C, 87·6; H, 4·8%), $\nu_{max.}$ 1770, 1680, and 1594 cm^{-1}.

Pyrolysis of the Adduct (XIII).—Pyrolysis of the adduct was carried out under the conditions described for (IX). In this case, 1,4-diphenyltriphenylene (X) was isolated in

[8] O. Diels and K. Alder, *Ber.*, 1929, **62**, 2337.
[9] W. Dilthey, I. ter Horst, and W. Schommer, *J. prakt. Chem.*, 1935, **143**, 189.
[10] K. Mackenzie, *J. Chem. Soc.*, 1960, 473.

70% yield upon chromatography. No other products were obtained.

Reaction between the Dimethyl Ether (XV) *and* 3,6-*Di*-(2-*pyridyl*)-s-*tetrazine* (VII).—The course of the reaction between the ether (XV) (24·2 mg) and the tetrazine (VII) (23·6 mg) in [^{2}H]chloroform (0·5 ml) was followed by n.m.r. spectroscopy. Signals due to starting materials diminished with concomitant evolution of nitrogen and formation of new peaks. Those observed first were due to the adduct (XVI), which reached maximum intensity before being themselves replaced by signals due to the isomer (XVII). The sample was added to chloroform–water and shaken. The chloroform layer was dried and evaporated to give 2,4a,5,12-*tetrahydro*-6,11-*dimethoxy*-1,4-*di*-(2-*pyridyl*)-5,12-*methanoanthra*[2,3-d]*pyridazine* (XVII) (40 mg), m.p. 180° (decomp.) (from ethanol) (Found: C, 75·3; H, 5·2; N, 11·9. $C_{29}H_{24}N_4O_2$ requires C, 75·6; H, 5·2; N, 12·2%), $\nu_{max.}$ 3360 and 1590 cm^{-1}, τ 0·60 (1H, s, NH, D_2O-exchangeable), 1—2·8 (12H, m, ArH), 4·75 (1H, s, bridgehead H), 5·23 (1H, s, bridgehead H), 5·60 (3H, s, OCH_3), 5·86 (3H, s, OCH_3), 7·06 (1H, s, *endo*-H), and 7·92 and 8·42 (2H, dd, *J* 9 Hz, CH_2).

Reaction between the Quinol Dimethyl Ether (XV) *and the Dienone* (VI).—The dimethyl ether (4·6 g) and the dienone (4·75 g) were heated under reflux in chlorobenzene (200 ml) for 50 h. Evaporation yielded 4a,5,12,12a-*tetrahydro*-6,11-*dimethoxy*-1,4-*dimethyl*-2,3-*diphenyl*-5,12-*methanotetracene* (XVIII) (8·4 g), m.p. 195—196° (from chloroform–petroleum) (Found: C, 86·5; H, 6·4. $C_{35}H_{32}O_2$ requires C, 86·8; H, 6·6%), $\lambda_{max.}$ 238 and 299 nm (log ε 4·88 and 3·94), $\nu_{max.}$ 1640, 1610, 1088, and 1039 cm^{-1}, τ 1·87 (2H, m, ArH), 2·55 (2H, m, ArH), 3·09 (10H, m, ArH), 5·95 (8H, s, OCH_3 and bridgehead CH), 7·19 (2H, s, *endo*-CH), 7·55 and 8·17 (2H, dd, *J* 9 Hz, CH_2), and 8·28 (6H, s, CMe).

Pyrolysis of the Diene (XVIII).—The compound (0·9 g) in a sublimation apparatus was immersed in an oil-bath preheated to 305° and allowed to melt for 2 min under nitrogen. The bath temperature was reduced and the pyrolysate sublimed to yield a pale yellow solid (0·8 g) which was chromatographed. Elution with light petroleum (b.p. 60—80°) gave 3′,6′-*dimethyl*-o-*terphenyl* (0·43 g), identical (m.p. and mixed m.p.) with authentic material. Elution with benzene yielded 4,9-*dimethoxybenz*[f]*indene* (III; R^1 = H, R^2 = Me) (0·38 g), m.p. 105° (from methanol) (Found: C, 79·6; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%), $\lambda_{max.}$ 251, 301, 311, and 347 nm (log ε 4·57, 3·93, 3·91, and 3·28), $\nu_{max.}$ 1630, 1607, 1170, and 1090 cm^{-1}, τ 1·83 (2H, m, ArH), 2·54 (2H, m, ArH), 2·86 (1H, dt, *J* 5·8 and 2 Hz, C=CH), 3·49 (1H, dt, *J* 5·8 and 2 Hz, C=CH), 5·99 (6H, s, OCH_3), and 6·40 (2H, t, *J* 2 Hz, CH_2).

2,3,4a,5,8,8a-*Hexahydro*-6,7-*dimethylbenz*[f]*indene*-4,9-*quinone* (XXIII).—A solution of 2,3-dimethylbutadiene (3 ml) and the quinone (XXII) (0·55 g) in dry benzene was heated under reflux for 20 h. The solvent was evaporated off to yield the *adduct* (XXIII) (0·83 g), m.p. 139—140° [from light petroleum (b.p. 60—80°)] (Found: C, 78·4; H, 7·8. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%), $\lambda_{max.}$ 261 nm (log ε 3·99), $\nu_{max.}$ 1670 and 1619 cm^{-1}, τ 6·84 (2H, m, CH·CO), 7·25 (4H, m, CH_2·CH_2·C=C), 7·83 (6H, m, CH_2·CH_2·C=C and CH_2·CH), and 8·38 (6H, s, CH_3).

Enolisation of the Adduct (XXIII).—2M-Sodium hydroxide (0·5 ml) was added to a solution of the adduct (0·75 g) in methanol (45 ml). The mixture was stirred for 10 min, then adjusted to pH 6 with dilute hydrochloric acid, and the solid was filtered off and dried to yield 2,3,5,8-*tetrahydro*-6,7-*dimethylbenz*[f]*indene*-4,9-*diol* (XXV) (0·70 g, 94%), m.p. 300° (from methanol) (Found: C, 78·2; H, 7·8. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%), $\lambda_{max.}$ 284 nm (log ε 3·4), $\nu_{max.}$ 3290 and 1123 cm^{-1}. The filtrate yielded the quinone (XXIV; R = H) (0·04 g).

Oxidation of the Diol (XXV) *to the Quinone* (XXIV; R = H).—A solution of sodium nitrite (1·1 g) in water (1·7 ml) was added dropwise to a stirred solution of the quinol (XXV) (0·68 g) in glacial acetic acid (30 ml) at 100°. After the evolution of gas had ceased, the temperature was lowered to 70° and sodium dichromate (1 g) in water (0·7 ml) was added together with a drop of concentrated sulphuric acid. The resulting solution was kept at 70° for an additional hour and then poured into iced water (150 ml). The yellow 2,3-*dihydro*-6,7-*dimethylbenz*[f]*indene*-4,9-*quinone* was filtered off (0·62 g), m.p. 150—151° (from methanol) (Found: C, 79·5; H, 6·1. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·1%), $\lambda_{max.}$ 254, 258, 281, and 347 nm (log ε 4·33, 4·37, 4·19, and 3·45), $\nu_{max.}$ 1660 and 1624 cm^{-1}, τ 2·31 (2H, s, ArH), 7·12 (4H, t, *J* 7 Hz, CH_2·CH_2·CH_2), 7·65 (6H, s, CH_3), and 7·9 (2H, m, CH_2·CH_2·CH_2).

Oxidation of the Quinol (XXV) *to the Quinone* (XXVI).—Silver oxide (1 g) was added to a solution of the quinol (XXV) (0·18 g) in dry benzene (20 ml) and the mixture was shaken for 2 h. Filtration followed by evaporation gave 2,3,5,8-*tetrahydro*-6,7-*dimethylbenz*[f]*indene*-4,9-*quinone* (XXVI) (0·17 g), m.p. 110° (decomp.) (from methanol) (Found: C, 78·8; H, 7·1. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0%), $\lambda_{max.}$ 261, 271, and 343 nm (log ε 4·19, 4·20, and 2·89), $\nu_{max.}$ 1655, 1644, and 1620 cm^{-1}, τ 7·03 (2H, s, >C=C·CH_2·C=C<), 7·21 (4H, t, *J* 7·2 Hz, CH_2·CH_2·CH_2), 7·94 (2H, m, CH_2·CH_2·CH_2), and 8·28 (s, CH_3). The quinone darkens on exposure to light or air.

Bromination of the Quinone (XXIV; R = H). A solution of the quinone (XXIV; R = H) (32 mg) and *N*-bromosuccinimide (26 mg) in carbon tetrachloride (10 ml) was heated in the presence of benzoyl peroxide (2 mg) for 15 min. Succinimide was filtered off and the solution was evaporated at room temperature under reduced pressure to leave a yellow crystalline mass which decomposed on exposure to the atmosphere. Rapid recrystallisation from methanol yielded 1-bromo-2,3-dihydro-6,7-dimethylbenz-[*f*]indene-4,9-quinone (XXIV; R = Br) (10 mg), m.p. 140—150° (decomp.), $\nu_{max.}$ 1660, 1597, 1339, and 740 cm^{-1}, τ 2·12 (2H, s, ArH), 4·50 (1H, t, *J* 6 Hz, C*H*Br·CH_2), 7·00 (2H, m, CH_2), 7·42 (2H, m, CH_2), and 7·58 (6H, s, CH_3). No reliable elemental analysis could be obtained for this compound, owing to its instability.

Reductive Acetylation of the Quinone (XXIV; R = H).—Zinc dust (100 mg) was added to a solution of the quinone (100 mg) in acetic anhydride (3 ml). The mixture was rapidly stirred for 30 min at 90°, filtered hot, and treated with hot water (40 ml) and allowed to cool. 2,3-*Dihydro*-6,7-*dimethylbenz*[f]*indene*-4,9-*diyl diacetate* (XXVII; R = H) was filtered off (130 mg), m.p. 159° (from methanol) (Found: C, 72·9; H, 6·3. $C_{19}H_{20}O_4$ requires C, 73·0; H, 6·5%), $\lambda_{max.}$ 232, 258, 268, 277, 286, and 296 nm (log ε 4·08, 3·52, 3·64, 3·78, 3·82, and 3·67), $\nu_{max.}$ 1752 and 1150 cm^{-1}, τ 2·52 (2H, s, ArH), 7·08 (4H, t, *J* 7 Hz, ArCH_2·CH_2), 7·57 (6H, s, CH_3), 7·60 (6H, s, CH_3), and 7·90 (2H, m, ArCH_2·CH_2).

Bromination of the Diacetate (XXVII; R = H).—*N*-Bromosuccinimide (0·59 g) and the diacetate (1 g) in carbon tetrachloride (50 ml) were heated under reflux in the presence of benzoyl peroxide (12 mg) for 30 min. After removal of the succinimide, the solution was evaporated to

yield (XXVII; R = Br) as a white gum which did not crystallise, τ 2·48 (2H, s, ArH), 3·42 (1H, t, *J* 4 Hz, CHBr), 6·98 (2H, m, CH_2), 7·32 (2H, m, CH_2), 7·49 (3H, s, CH_3), 7·54 (3H, s, CH_3), and 7·60 (6H, s, 2 × CH_3).

Dehydrobromination of the Bromide (XXVII; R = Br).—The bromo-diacetate (XXVII; R = Br) was dehydrobrominated without further purification. Anhydrous lutidine (30 ml) was added to the crude gum (0·65 g), together with *p*-t-butylcatechol (0·30 g) to inhibit polymerisation. The resulting solution was heated on a water-bath for 45 min, then poured into water (500 ml). A purple solid was filtered off and dried. Sublimation gave *6,7-dimethylbenz*[f]*indene-4,9-diyl diacetate* (III; R^1 = Me, R^2 = Ac) (0·31 g) as white needles, m.p. 174·5—175° (from methanol) (Found: C, 73·2; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%), $\lambda_{max.}$ 234, 243, 251, 286, 296, and 309 nm (log ε 4·59, 4·54, 4·53, 3·90, 4·00, and 3·90), $\nu_{max.}$ 1754, 1655, and 1626 cm^{-1}, τ 2·48 (2H, s, ArH), 3·23 (1H, dt, *J* 5·8 and 2 Hz, CH=CH), 3·51 (1H, dt, *J* 5·8 and 2 Hz, CH=CH), 6·62 (2H, t, *J* 2 Hz, CH_2), 7·57 (3H, s, CH_3), 7·59 (3H, s, CH_3), and 7·63 (6H, s, 2 × CH_3).

Hydrolysis of the Diacetate (III; R^1 = Me, R^2 = Ac).—A mixture of the diacetate (60 mg), aqueous 10% potassium hydroxide (3 ml), and ethanol (1 ml) was heated under reflux for 45 min. The cooled red solution was neutralised with dilute acetic acid. A black precipitate was filtered off and chromatographed with chloroform as eluant. A yellow crystalline compound (6 mg) was the only product isolated and was shown to be 2,3-dihydro-6,7-dimethylbenz[*f*]indene-4,9-quinone by comparison (m.p., mixed m.p., i.r. and mass spectra) with authentic material.

Financial support from the Council of the University of Cape Town and the Council for Scientific and Industrial Research is gratefully acknowledged.

[3/1139 *Received, 4th June,* 1973]