

585. *The Stereochemistry of the Adducts of p-Benzoquinone with two Molecules of Cyclopentadiene. Charge-transfer from Olefinic Double Bonds to p-Benzoquinone and Ene-1,4-dione Groups.*

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The *endo-trans-endo*-configuration of the bicyclopentadiene-benzoquinone adduct has been established by photochemical cyclisation, in agreement with Winstein's conclusions. *p*-Benzoquinones and ene-1,4-diones with olefinic double bonds overlapping the chromophore show a new band in the ultraviolet spectrum, not present in that of the parent chromophore, attributed to intramolecular charge-transfer. The medium-wavelength band in the spectrum of *p*-benzoquinones is very sensitive to the effects of strain.

AN interest in their use for the study of photochemical reactions and electronic spectra led us to examine critically the evidence for the stereochemistry of the mono-¹ and bis-adducts ² of cyclopentadiene with *p*-benzoquinone. The *endo*-configuration of the mono-adduct (I) was simply confirmed by its isomerisation by light to the cage-isomer ³ (II).

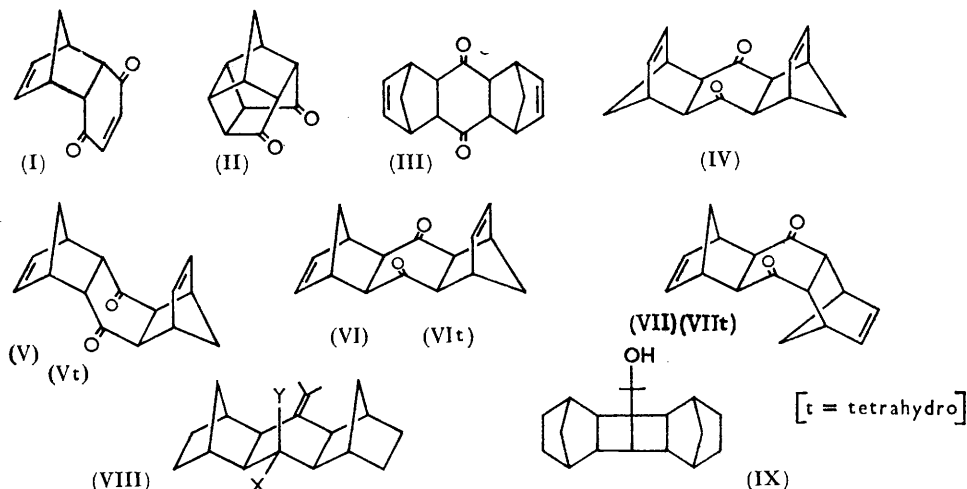
¹ Albrecht, *Annalen*, 1906, **348**, 34; Diels, Blom, and Kroll, *ibid.*, 1925, **443**, 247; Diels and Alder, *ibid.*, 1928, **460**, 98; 1930, **478**, 141.

² Alder and Stein, *Annalen*, 1935, **501**, 247.

³ Cookson, Crundwell, and Hudec, *Chem. and Ind.*, 1958, 1003.

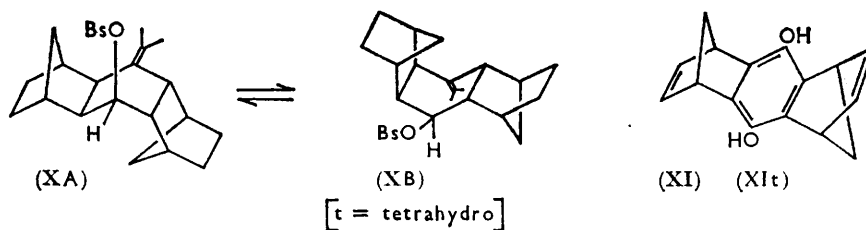
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The bisadduct (III) is formed by addition of a second molecule of cyclopentadiene to the monoadduct (I). Of the four possible structures Alder and Stein² preferred the *endo-cis-endo* (IV), and later workers (e.g., ref. 4) seem to have accepted this assignment. The evidence, however, was far from conclusive, and some of it was rather more consistent with the *endo-trans-endo*-configuration (V) (a fuller discussion is given in ref. 5), which consideration of steric and electronic factors would have predicted. Alder and Stein² isomerised the tetrahydro-derivative, m. p. 245°, of the bisadduct to a compound, m. p. 225°, and Winstein⁴ later described a third stereoisomer, m. p. 164°. By reaction with



isopropyl-lithium and dehydration, the third isomer was converted into an unsaturated ketone (VIII; XY = O), which was reduced to an alcohol, assigned structure (VIII; X = OH, Y = H). Solvolysis of the *p*-bromobenzenesulphonate of the alcohol yielded a saturated alcohol, given the interesting bicyclohexane structure (IX). This again was rather suspicious, for the more probable direction of ketone reduction would have given the epimer (VIII; X = H, Y = OH), whose sulphonate would not have been expected to solvolyse with participation of the double bond (but see ref. 6 and later for revision). On the other hand, if (V) represents the initial adduct, Alder and Stein's isomer, m. p. 225°, would become (VI_t) and Winstein's, m. p. 164°, (VII_t). The sulphonate derived from the last would have structure (X), solvolysis of which in conformation (XB) would more plausibly involve the double bond.

With these thoughts in mind we set out to prove the configuration of the bisadduct* (V) and its isomers, making use of photochemical cyclisation³ to demonstrate *endo*-ring



fusions [cf. (I) → (II)]. The idea was to make the same cage compound by two alternative routes. Treatment of the adduct (V) with selenium dioxide gave a pale yellow

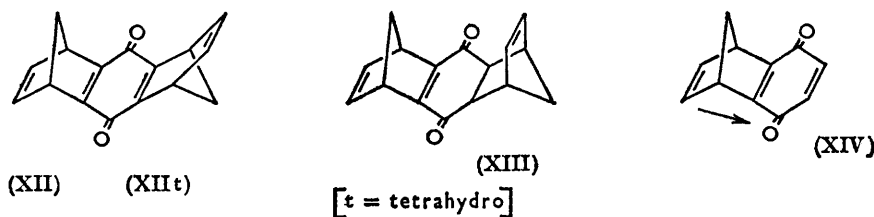
* Corrected stereochemistry is shown from now on.

⁴ Winstein, *Experientia*, Sup. II, 1955, 137.

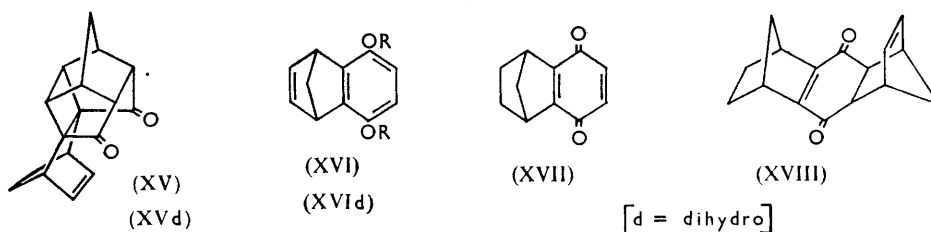
⁵ Hill, Ph.D. Thesis, Southampton, 1961, Ch. III.

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substance in 15% yield, betrayed as an ene-1,4-dione by its spectra (ν_{\max} 1655, 1603, and 1564 cm^{-1} ; λ_{\max} 264 $\text{m}\mu$, ϵ 6400) and chemical properties. In the presence of very dilute base the enedione rapidly isomerised to the quinol (XI), which could be oxidised to the quinone (XII). In further confirmation of structure (XIII), sublimation at 150°/20 mm. was accompanied by cracking to cyclopentadiene and the quinone (XIV). Irradiation of the enedione (XIII), either in solution or in the crystalline state, converted it in good yield into an isomer with the infrared and ultraviolet spectra expected for the cage compound (XV). It took up one molecule of hydrogen, forming the saturated diketone (XVd).



The monoadduct (I) was then transformed into the quinone (XVII) of the dihydro-series by the steps, (I) \rightarrow (XVI; R = Ac) \rightarrow (XVI d; R = Ac) \rightarrow (XVI d; R = H) \rightarrow (XVII). Addition of cyclopentadiene to the quinone (XVII) gave an adduct (XVIII), isolated in 60% overall yield from (I). Irradiation then gave a saturated isomer of the adduct, identical in all respects with the cage compound (XVd), made from (I) by the previous route through (V) and (XIII). While it might be rash to be too categorical in choosing the configuration (V) from the four possible modes of addition of cyclopentadiene to (I), no such reservations apply to the addition to the quinone (XVII). The photocyclisation proves that the adduct has the *endo*-configuration. The quinone ring



must be at least approximately planar, so that the only significant difference between the two alternative transition states for *endo*-addition is the relative hindrance of the methane or ethane bridges: undoubtedly the latter will predominate. Since, therefore, this adduct must have the configuration (XIII), the bisadduct of cyclopentadiene and benzoquinone must be (V). At this point we informed Professor Winstein of our results, and soon afterwards a preliminary Note⁶ announced his own rigorous proof of the structure (V).

Treatment of the bisadduct (V) with alkali in the absence of air gave the *endo-cis-exo*-isomer (VI), m. p. 184°, in 45% yield, together with an isomer of very high melting point (15%), the structure of which will be discussed in a later Paper. When the adduct (V) was treated with alkali in air, oxidation accompanied the isomerisation with formation of considerable amounts of the quinone (XII) and quinol (XI). Boiling dilute alkali in the absence of air (but working up and chromatography in its presence) turned the tetrahydro-derivative (Vt) into a mixture of the isomers (VI t) (40% yield) and (VII t) (18%) with the quinone (XII t) (10%) and quinol (XI t) (5%). There was also present (10%) a white crystalline substance (m. p. 266–268°) of unknown structure which gave a correct analysis for (XII t) plus two oxygen atoms and showed a multiplicity of bands in the carbonyl stretching region (1660, 1682, 1715, 1730, and 1753 cm^{-1}) and maxima in the ultraviolet

⁶ Winstein, de Vries, Heck, and Piccolini, *Chem. and Ind.*, 1959, 1416.

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at 210 (ϵ 7500) and 305 $m\mu$ (ϵ 52). One possible structure would be the diepoxide of the quinone (XII t). The quinone (XII t) itself may well be an intermediate, for some of the high-melting compound was formed (10%) when it was treated with alkali in air.

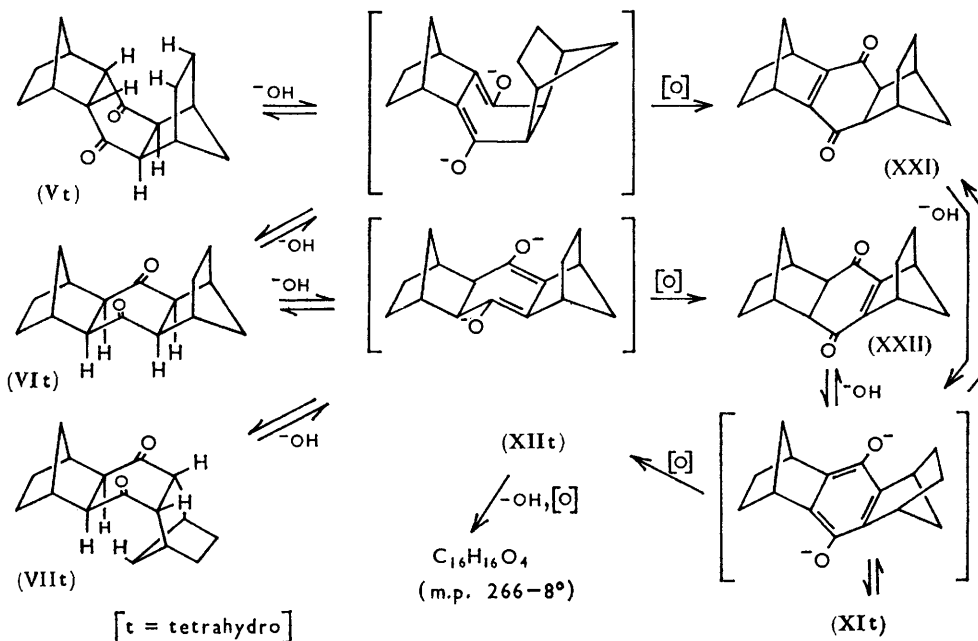
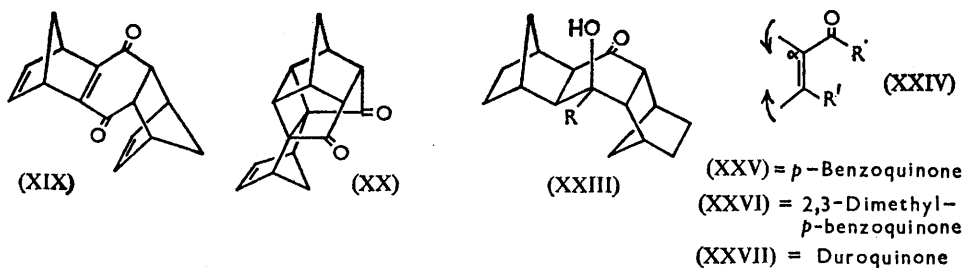


Chart.

The processes involved in the autoxidation⁷ and isomerism of (V t) are summarised in the Chart. This scheme is confirmed by the isolation of all the intermediate compounds shown. The two enediones, (XXI) and (XXII), were not isolated from the treatment of (V t) with dilute alcoholic potassium hydroxide, as were the rest of the compounds, but were obtained in small quantities during unsuccessful attempts to convert it and (VI t) into $\gamma\delta$ -unsaturated ketones, analogous to (VIII), with alkyl-lithium reagents and subsequent dehydration. They were characterised by their infrared and ultraviolet spectra and by analysis.

The results of the alkyl-lithium experiments serve to demonstrate the steric difference to the approach of a reagent to the two sides of a bicyclo[2,2,1]heptane ring. Thus,



although Winstein⁴ succeeded in preparing alcohols of the type (XXIII) from the *exo-trans-exo*-isomer (VII t), we failed to observe any evidence of the reagent attacking a carbonyl group in the other two isomers, where at least one *endo*-configuration was present.

¹ Cf. Dauben, Boswell, and Templeton, *J. Org. Chem.*, 1960, **25**, 1853.

In order to remove the labile tertiary hydrogen atoms α to the carbonyl groups in (VII t), and thus prevent attack at the carbonyl groups themselves, the incoming nucleophile must overcome a greater steric barrier in the form of an ethano-bridge rather than the smaller methano-bridge in the isomers we tried. Evidence that enolisation was indeed occurring in (V t) and (VI t) was furnished by the isolation of the enediones, (XXI) and (XXII), and the quinone (XII t), when air was allowed to reach the reaction mixture.

The spectroscopic features of the three isomers (Table 1) confirm the expected differences in geometry of the cyclohexanedione rings. In (V t) the ring must be almost planar as

TABLE 1 (see CHART).

	(V t)	(VI t)	(VII t)
$\nu_{\max.}$ C=O (cm. ⁻¹) in CHCl ₃	1686	1698	1692
$n \longrightarrow \pi^*$ C=O $\lambda_{\max.}$ (m μ) (ϵ) in cyclohexane	308 (26)	292 (31)	306 (43)

non-bonded repulsions are at a minimum in this conformation. A slight departure from planarity would be allowed in (VII t) where the repelling hydrogen atoms are staggered, and in (VI t) the ring should have the conventional boat form. This variation in conformation results in the C-CO-C bond angles increasing, and therefore the CO bond orders, stretching frequencies, and $n \longrightarrow \pi^*$ absorption frequencies decreasing in the order (VI t), (VII t), (V t), which is the observed trend.

To obtain more enediones for spectroscopic study, and as a possible entry into the series of stereoisomers inaccessible by epimerisation of the adduct (V) in which the methylene bridges are on the same side of the molecule (*e.g.*, IV), we examined the addition of cyclopentadiene to the quinone (XIV). Infrared spectroscopy of the product suggested that it was a mixture of two ene-1,4-diones, the minor component being the isomer (XIII) already encountered. Although the isomers were very hard to separate, extensive chromatography and recrystallisation finally yielded a fairly pure sample of the new isomer. It melted some 2° higher than the old one (XIII) and had a very similar i.r. spectrum: the most noticeable difference being in the out-of-plane bending frequencies, at 730 and 692 cm.⁻¹ in (XIII), but at 712 and 722 cm.⁻¹ in the new isomer, which also lacked the rather weak band at 1171 cm.⁻¹ that occurred in (XIII). There were also significant differences in the u.v. spectra, especially in the absorption attributed to transannular charge-transfer (discussed later), and in the X-ray powder photographs. The quinol and quinone made from the new isomer had spectra extremely similar to those from (XIII)—since they melt with decomposition, these pairs of compounds cannot be compared by mixed melting point.

There seems no doubt, then, that the major product from the reaction was one of the other three possible stereoisomers of (XIII). That it was the alternative *endo*-adduct (XIX) follows from its photoisomerisation to a cage compound (XX), which depressed the melting point of (XV). (Pyridine solutions of the two photoisomers gave distinct p.m.r. spectra.) This probably constitutes the first representative of the isomers with two *cis*-bicycloheptene units—Winstein's B series.

The much greater preference for addition of cyclopentadiene to the concave side of the dienophile (XIV) than (XVII) is probably mainly a reflection of the reduced repulsion between the cyclopentadiene molecule and the π -electrons of the double bond in (XIV) than the *endo*-C-H bonds in (XVII). In addition the dipole moment that would be produced by any charge-transfer from the olefinic double bond to the quinone group in (XIV—see arrow) would also tend to attract the diene to the concave face.⁸

Absorption Spectra

One of the main motives behind this work was an interest in the effect of unconjugated but interacting double bonds on the electronic spectra of the *p*-benzoquinone and ene-1,4-dione chromophores. Compounds containing the latter were readily available as Diels-Alder adducts (and their derivatives) of dienes with *p*-benzoquinones, and, in general, the

⁸ Berson, Hamlet, and Mueller, *J. Amer. Chem. Soc.*, 1962, **84**, 297.

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corresponding quinones could be synthesised from these by base-catalysed isomerisation to the quinols and subsequent oxidation, *e.g.*, cyclohexa-1,3-diene + *p*-benzoquinone \longrightarrow (XXXI) \longrightarrow (XL) \longrightarrow (XXVIII). Analysis of the spectra revealed two dominant effects: ring strain and intramolecular charge-transfer.†

Quinones.—*p*-Benzoquinone has three distinct regions of absorption above 220 $m\mu$, which have been labelled I, II, and III in order of increasing wavelength.⁹ Band I, an intense absorption at 245 $m\mu$ ($\log \epsilon$ 4.2) is believed to be analogous to the $\pi \longrightarrow \pi^*$ absorption of $\alpha\beta$ -unsaturated ketones. Band II, at 285 $m\mu$ ($\log \epsilon$ 2.5) is also a $\pi \longrightarrow \pi^*$ transition but formally forbidden, and band III constitutes the weak $n \longrightarrow \pi^*$ absorption of the carbonyl groups.^{9,10} All three transitions are polarised in the same direction. Consequently, the two forbidden ones, II and III, acquire their intensity by mixing with I. Of the two $\pi \longrightarrow \pi^*$ transitions, II appears to be most sensitive to substituent effects, both electronic and, as we shall demonstrate, ring strain. For example, substitution by methoxyl in the *p*-benzoquinone ring moves both $\pi \longrightarrow \pi^*$ absorptions to longer wavelength, but the shift for band II is eight times that for band I.¹¹ Such substitution tends to move the $n \longrightarrow \pi^*$ band hypsochromically, with the result that in many *p*-quinones the latter is partially or entirely hidden beneath the longer wavelength $\pi \longrightarrow \pi^*$ absorption.

It has been known for some time that as the angle α , *e.g.*, in (XXIV), is decreased, the $\pi \longrightarrow \pi^*$ absorption of the chromophore O=CR=C=CR' moves bathochromically.¹² Hence, by substitution such as in (XVII) we may expect the *p*-quinone band I to be so affected, and furthermore, by analogy with other effects which move this absorption bathochromically, a much larger shift of band II should be observed. Little is known of the effects of ring strain on $n \longrightarrow \pi^*$ transitions. However, the tendency for this transition of the azo-group to move hypsochromically with increasing ring strain has been observed by Cohen and Zand.¹³

Results. The ultraviolet spectra of the quinones (XII), (XII_t), XIV), (XVII), and (XXV)—(XXX) were measured in ethanol and cyclohexane. Our detailed analyses of the curves are given in Table 2 and a few, which illustrate the most interesting features of the series, are depicted in Figs. 1 and 2.

(a) Band I ($\pi \longrightarrow \pi^*$). Except for *p*-benzoquinone itself, this intense band is always observed as a doublet, whose resolution is favoured by the less polar solvent. Solvent shifts (which here and hereafter refer to movement of band maxima from cyclohexane to ethanol as solvent) are slight, 1 or 2 $m\mu$, and towards the red. This is accompanied by a drop in intensity. The strain displacements amount to 9 $m\mu$ in the disubstituted, (XXVI) against (XVII), and about 25 $m\mu$ in the tetrasubstituted quinones (XXVII) against (XII_t). Smaller increases in strain caused by the introduction of unsaturation produce barely perceptible shifts in this band, but successive decreases in intensity are very noticeable.

(b) Band II ($\pi \longrightarrow \pi^*$). The sensitivity of this band to substituent effects is considerable, as demonstrated by the fact that in the series of compounds which have been measured, its maximum occurs within a range of 135 $m\mu$. Firstly a red shift of about 40 $m\mu$ is observed on di- or tetra-alkyl substitution of *p*-benzoquinone. Introduction of strain produces a further displacement of almost 30 $m\mu$ in the unsymmetrical, (XXVI) against (XVII), and 50 $m\mu$ in the symmetrical case, (XXVII) against (XII_t). The band

† Strictly speaking, all the local *p*-quinone transitions involve transfer of charge and therefore may be labelled intramolecular charge-transfer. However, as the phenomenon to be described later is analogous to the intermolecular charge-transfer involved in molecular complexes, the use of the phrase will be restricted to transitions between *classically* non-conjugated chromophores.

⁹ Brand and Goodwin, *Trans. Faraday Soc.*, 1957, **53**, 295.

¹⁰ (a) Sidman, *J. Amer. Chem. Soc.*, 1956, **78**, 4567; (b) Sidman, *J. Chem. Phys.*, 1957, **27**, 820.

¹¹ Flaig, Salfeld, and Baume, *Annalen*, 1958, **618**, 820.

¹² (a) Jones, Mansfield, and Whiting, *J.*, 1956, 4073; (b) Schubert and Sweeny, *J. Amer. Chem. Soc.*, 1955, **77**, 2297; (c) Wheeler, *ibid.*, 1956, **78**, 3216; (d) Chandross and Yates, *Chem. and Ind.*, 1960, 149.

¹³ Cohen and Zand, *J. Amer. Chem. Soc.*, 1962, **84**, 586.

TABLE 2.
 Ultraviolet spectra of substituted *p*-benzoquinones.^a

Compd.	Solv. ^o	Band I	c-t	Band II	Band III
(XXV) ^b	CH	242 (17,900)		285 (420)	434 (20) 457 (20) 479 (12)
		Et		296 (425)	435 (19)
(XXVI) ^c	H	246 (17,000)		327 (1070)	426 (24) 439 (24)
		252 (14,100)			445 (25) 432 (30)
	Et	248 (16,500) 254 (16,000)		334 (400)	
(XVII)	CH	255 (15,500)		355 (800)	435 ^d (26) —480
		263 (14,000)			445 ^d (52)
	Et	256 (15,500) 263 (13,700)		360 (700)	
(XIV)	CH	257 (14,500)	307 (260)	385 (520)	448 ^d (50) 472 ^d (30) 500 ^d (14) 541 ^d (11)
		264 (13,500)			Buried
(XXVIII)	CH	258 (11,700)	295—305 ^d (530)	386 (440)	
		243 ^d (12,500) 252 (16,000) 260 ^d (14,000)	302 ^d (350)	356 (700)	435 (25) 455 (24) 472 ^d (16)
	Et	252 (14,700) 261 ^d (13,000)	302 ^d (350)	363 (500)	450 ^d (17)
(XXVII) ^b	H	258 (21,000)		330 (210)	432 (25)
		264 (20,500)			
	Et	258 (21,000) 265 (20,000)		340 (240)	430 ^d (37)
(XII ^t)	CH	279 (15,400)		379 (188)	441 ^d (40) 463 ^d (28)
		287 (18,200)			Buried
(XXIX)	Et	287 (16,500)		389 (145)	
		278 ^d (14,300) 285 (16,500)	305—320 ^d (930)	406 (146)	441 ^d (79) 471 ^d (39) 505 ^d (16)
	Et	283 (13,900)	312—329 ^d (710)	370—420 ^d (170)	Buried
(XII)	CH	278 ^d (13,300)	345 (590)	420 (131)	470 ^d (59) 500 ^d (23)
		285 (14,900)			Buried
(XXX)	Et	288 (12,600)	300—357 (520)	400—445 (142)	
(XXX)	CH	257 (12,500)	336 ^d (117), 382 (102)		476 ^d (27)

^a λ_{\max} given in $m\mu$, extinction coefficients in parentheses. ^b Ref. 14. ^c Ref. 11. ^d Point of inflection. ^e CH, cyclohexane; Et, ethanol; H, n-hexane.

is moved to even longer wavelengths in both series by unsaturation of the bridged ring substituents: (XVII)—(XIV) 30 $m\mu$, (XII^t)—(XII) 41 $m\mu$. Although the last displacements are thought to be mainly due to increased strain, it must be appreciated that the electronic environment of the chromophore is now profoundly altered, *e.g.*, in (XII), and this is likely to have some influence on the parent transitions as well as producing a charge-transfer absorption (see below). Band II of the disubstituted quinone (XXVIII) occurs at 29- $m\mu$ shorter wavelength than that of (XIV), which is to be expected on account of the difference in strain in the two molecules.

The solvent shifts, again bathochromic, are slightly greater than those of band I.

(c) Band III ($n \rightarrow \pi^*$). As expected,¹⁵ alkyl substitution in *p*-benzoquinone results in a slight increase in the energy of this transition, which appears as a weak absorption at very long wavelengths, often exhibiting fine structure in non-polar solvents. Bathochromic displacements of band II begin to obscure band III in (XVII) and (XII^t), and because of its characteristic blue solvent shift, complete envelopment occurs in ethanol

¹⁴ Braude, *J.*, 1945, 490.

¹⁵ Sidman, *Chem. Rev.*, 1958, 58, 689.

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for (XIV), (XII), (XII_t), and (XXIX). However, despite these tendencies, a definite bathochromic displacement is discernible as the influence of strain and/or electronic interaction increases. Thus, in (XIV) a weak shoulder is observed as far into the visible region as 541 m μ . Intensities of the transition are not measurably enhanced because of the low charge-transfer intensities and the large energy difference and insufficient overlap between the relevant orbitals.¹⁶

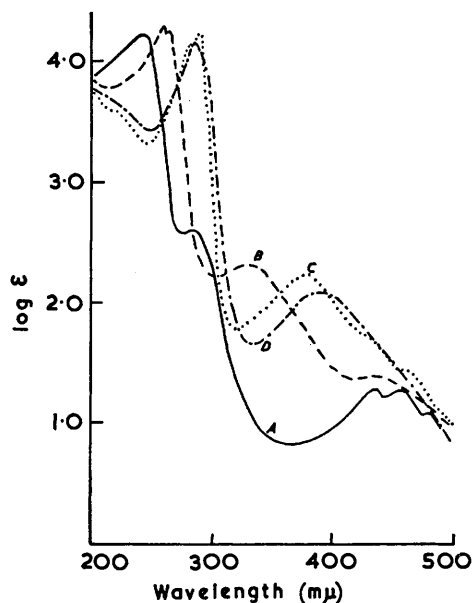


FIG. 1. Ultraviolet spectra of some *p*-quinones showing the effects of substitution and strain.

A, *p*-benzoquinone; B, duroquinone; C, (XII_t) (all in cyclohexane); D, (XII_t) in ethanol.

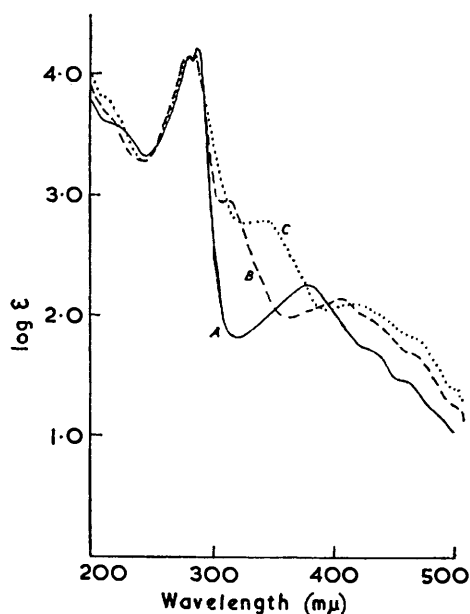


FIG. 2. Ultraviolet spectra of some *p*-quinones showing intramolecular charge-transfer.

A, (XII_t); B, (XXIX); C, (XII) (in cyclohexane).

(d) The charge-transfer transition. Comparison of the spectra of certain members of the series, *i.e.*, (XXV)—(XXVII), (XVII), (XII_t), with those of others, *i.e.*, (XIV), (XII), (XXVIII), (XXIX), and (XXX), reveals additional absorption in the latter at 300–350 m μ which must be a result of interaction between the bicycloheptene double bond(s) and the *p*-quinone group. As *p*-quinones are very ready electron acceptors, it seems highly

TABLE 3.

Charge-transfer maxima in chloroform (wavelengths in m μ).

	Maleic anhydride	Benzoquinone	Tetracyanoethylene
Cyclohexene	318	324	435
Cyclopentene	312	326	435
Bicyclo[2,2,1]heptene	<296	307	439

probable that such interaction consists of *intramolecular* charge-transfer. The energy required for this process, as observed from the spectra, is consistent with the value observed for benzene-*p*-benzoquinone *intermolecular* charge-transfer, *i.e.*, $\lambda(c-t) = 305 \text{ m}\mu$ ¹⁸

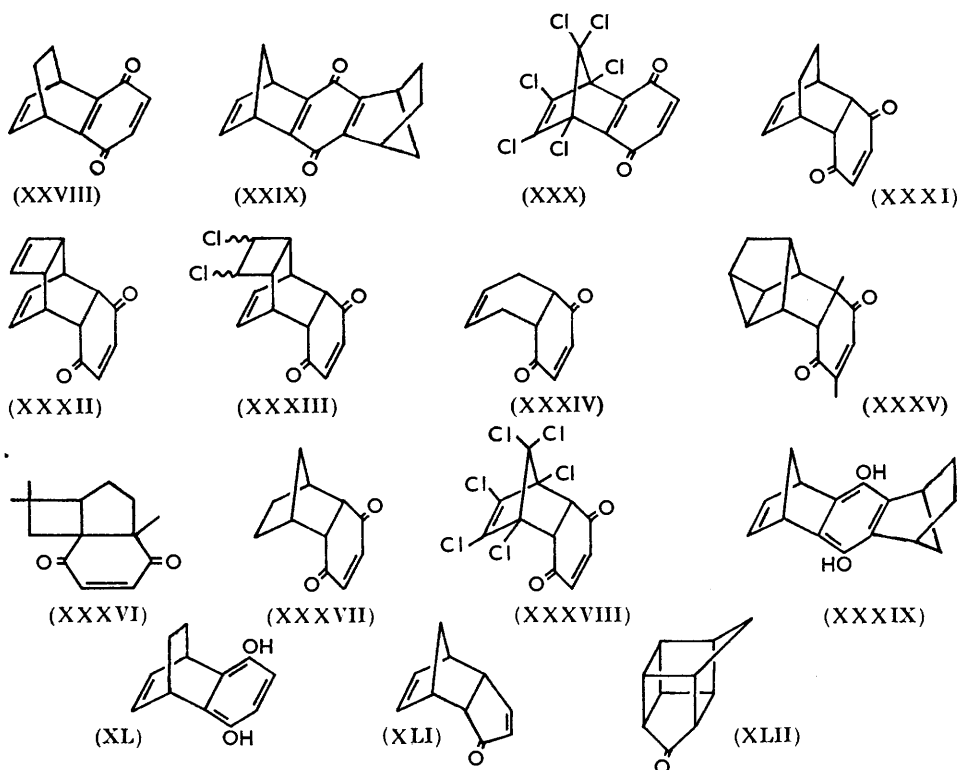
¹⁶ Mason, *Quart. Rev.*, 1961, 287.

¹⁷ Wilcox and Craig, *J. Amer. Chem. Soc.*, 1961, **83**, 4258.

¹⁸ Kuboyama and Nagakura, *J. Amer. Chem. Soc.*, 1955, **77**, 2644.

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(in *n*-heptane). The ionisation potentials of benzene and bicycloheptene must be of the same order, so one may expect intramolecular transitions such as those under discussion to lie in this region. Variation in the wavelength over a range of, say, 50 m μ , will depend



on such effects as symmetry, alkyl substitution, strain, and steric factors. As predicted,^{24a} the energy of the transition seems to be rather insensitive to the precise geometry of overlap. Although the steric and electronic complexity of the orbital systems make it difficult to account for the movement of the band within the series, the hypsochromic shifts found for (XIV) against (XXVIII) and (XXX) against (XIV) are consistent with the expected differences in the ionisation potentials of the donor parts of these molecules. The less strained bicyclo-octene double bond is, presumably, more reluctant to part with an electron than the bicycloheptene group, and it has been observed previously that certain chlorine substituted double bonds have lower ionisation potentials than their unsubstituted analogues.¹⁹

In spite of inconvenient stereochemistry for the process, the intensities of these absorptions are moderate. Probably, much of it is "borrowed" from the local $\pi \rightarrow \pi^*$ absorptions of donor and (because ground-state orbitals overlap^{24b}) acceptor parts of the molecules.¹⁷

Solvent shifts are slight (1–5 m μ) and to the red with decreasing intensity.

Any interaction between the quinonoid system and double bonds in other parts of the molecules in their ground-states is not reflected in the infrared C=C and C=O stretching frequencies (Table 4).

¹⁹ Walsh, *Trans. Faraday. Soc.*, 1945, **41**, 35.

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TABLE 4.
Infrared spectra of quinones in chloroform (frequencies in cm.⁻¹).

Compd.	C=O	C=C	C=C	$(\nu_1 + \nu_2)/2$ (C=O)	Compd.	C=O	C=C	C=C	$(\nu_1 + \nu_2)/2$ (C=O)
	Stretch	Stretch (quinone)	Stretch donor			Stretch (quinone)	Stretch donor		
(XXV)	1660	1595		1667	(XIV)	1652	1583	1561	1652
	1673				(XIIIt)	1641	1571		1644
(XXVI)	1633 *	1607		1646		1647			
	1658				(XXIX)	1644	1573	1557	1644
(XXVII)	1640	1608		1649	(XII)	1640	1579	1554	1644
	1658 *					1949 *			
					Bicyclo[2,2,1]heptene			1569	

* Point of inflection.

*Intermolecular charge-transfer.*²⁰ Calculation from the simple expression,²¹

$$h\nu = I - E - \Delta,$$

where ν is the frequency of the charge-transfer band, I is the ionisation potential of the donor, E the electron affinity of the acceptor, and Δ a constant for a series of closely related compounds, showed that the intermolecular charge-transfer transition from cyclohexene to *p*-benzoquinone should occur at 308 m μ [I of cyclohexene from ref. 22; ($E + \Delta$) from data¹⁸ for benzene-*p*-benzoquinone]. It was therefore gratifying to find the maximum in cyclohexane solution at 310 m μ , a value also in excellent agreement with the position of the band assigned to intramolecular charge-transfer in the unsaturated quinones.

The close numerical correspondence, however, is partly a matter of luck, for the maxima of the charge-transfer band of chloroform solutions of the olefins and electron acceptors given in Table 3 by no means simply follow the trends in I and E . (The 14-m μ longer wavelength absorption of cyclohexene-*p*-benzoquinone in chloroform than in cyclohexane is in line with the 10-m μ solvent shift for benzene-*p*-benzoquinone.^{18,23}) Presumably the deviations are due to lack of constancy in the omnibus term, Δ , taken as the difference in binding energy between donor and acceptor in the ground and excited states. Although variations in orientation of the components are expected to affect the intensity much more than the energy of the transition,²⁴ the latter must be raised by reduced overlap. The shorter wavelength of the maximum for bicyclo[2,2,1]heptene with *p*-benzoquinone or maleic anhydride than for cyclohexene or cyclopentene (expected to have higher I value) (Table 3) is probably due to this, because the two saturated bridges get in the way. At least in the complex of benzene and *p*-benzoquinone the two molecules are in parallel planes and on the same axis. Undoubtedly, part of the reason for the charge-transfer energy of the intramolecular case, *e.g.*, (XIV) being less than that of the bicycloheptene-*p*-benzoquinone system (and, in fact, nearer that of the cyclohexene-*p*-benzoquinone system) is that net orbital overlap is superior in the unsaturated quinone, because donor and acceptor are held close together in a rigid framework. In comparison between donor-acceptor systems so held, variations in orientation are eliminated.

Ene-1,4-diones.—The chromophore $O=\overset{|}{C}=\overset{|}{C}=\overset{|}{C}=\overset{|}{C}=O$ can be expected to exhibit absorption characteristics similar to that of an alkyl-substituted $\alpha\beta$ -unsaturated ketone,^{26,27} and indeed, this is what is observed.^{25,28} An intense $\pi \rightarrow \pi^*$ absorption occurs at 225 ± 5

²⁰ For review see Briegleb and Czekalla, *Angew. Chem.*, 1960, **72**, 401.

²¹ Orgel, *Quart. Rev.*, 1954, **8**, 437.

²² McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66.

²³ Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

²⁴ (a) Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839; (b) Murrell, *ibid.*, 1959, **81**, 5037; (c) White, *ibid.*, p. 2912.

²⁵ Present work.

²⁶ Gillam and Stern, "Electronic Absorption Spectroscopy," Arnold, London, 1954, Ch. 5.

²⁷ Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76.

²⁸ (a) Butz, Bastron, and Davis, *J. Org. Chem.*, 1942, **8**, 515; (b) Mandelbaum and Cais, *ibid.*, 1962, **27**, 2243.

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$m\mu$ and the characteristically weak carbonyl $n \rightarrow \pi^*$ band at $\sim 370 m\mu$. The latter is at somewhat longer wavelength than in an alkyl-substituted $\alpha\beta$ -unsaturated ketone because the energy of the first antibonding π -orbital is lowered by the electron-withdrawing power of the "substituent"¹⁵ and extended conjugation. The absorption is often very broad, and contains much resolvable fine structure, the maxima of which may lie over a range of as much as $60 m\mu$.

Results. The details of the absorption spectra of compounds (I), (XIII), (XVIII), (XIX), (XXI) [or (XXII)], and (XXXI)—(XXXVIII)] are given in Table 5, whilst a few of the curves which illustrate the main features of the study are presented in Figs. 3 and 4.

TABLE 5.
Ultraviolet spectra of ene-1,4-diones.^a

Compd.	$\pi \rightarrow \pi^*$		c-t		$n \rightarrow \pi^{*c}$	
	CH	Et	CH	Et	CH	Et
(I)	226 (12,900)	226 (13,000)	278 (248)	284 (254)	385 (58)	374 (63)
	238 ^b (6800)	239 ^b (8400)				
(XXXI)	223 (13,000)	227 (11,000)	267 ^b (320)	278 ^b (260)	388 (64)	371—381 (60)
(XXXII)	223 (12,000)	224 (11,200)	262—280 ^b (440—280)	268—287 ^b (400—250)	386, 392 (66)	370—386 (67)
(XXXII)†		224 (11,200)	263—286 ^b (410—240)			382 ^b (63)
(XXXIII)†		223 (12,200)	258—281 ^b (445—210)			381 (62)
(XXXIV)	223 (11,000)	223 (10,600)	253—263 ^b (320)	257 ^b (400)	372 (55)	361 (62)
	233 ^b (7600)					
(XXXVIII)	229 ^b (10,600)		278 (107)		389 (62)	
	239 ^b (5000)					
(XXXV)	233—238 (14,100)	235 ^b (13,000)			385 (75)	374 (77)
		240 (13,500)				
(XXXVI)	225 (14,000)	225 (14,700)			372—389 (100)	372 (100)
	237 ^b (5600)	237 ^b (9700)				
(XXI) or (XXII)	264 (8000)	267 (> 6400)			370 (70)	
(XVIII)	269 (8300)	272 (8800)	"Buried" or responsible for		386 (77)	370—385 (81)
	279 (5300)					
(XIII)	264 (6400)	268 (5700)	306 (1360)	300—315 (1150)	389 (73)	396 ^b (80)
(XIX)	261 (6400)	266 (6100)	286—299 ^b (1650)	293—312 ^b (1730)	389 (76)	391 ^b (86)

^a λ_{\max} given in $m\mu$, extinction coefficients in parentheses. ^b Point of inflection. ^c Shows fine structure, main maxima quoted. † In CH_3CN .

(a) Enedione $\pi \rightarrow \pi^*$ transition. This intense absorption lies at $225 \pm 5 m\mu$ for the unsubstituted compounds and suffers bathochromic displacement on alkyl substitution which, in (XXXV), is strictly analogous to an $\alpha\beta$ -unsaturated ketone. However, in (XIII), (XVIII), (XIX), and (XXI) or (XXII), where the system is disubstituted, the shift is greater than what would be expected by this analogy, *i.e.*, to $254 \pm 5 m\mu$.²⁷ The extra $10\text{--}15 m\mu$ which is observed can be attributed to the strain factor discussed for the quinones (above). A marked drop in intensity [which in (XIII) and (XIX) amounts to 50%] accompanies the shift. Such reduction in the intensity of the local transition of the acceptor chromophore has been observed before in cases where intramolecular charge-transfer occurs (see ref. 12*a* and later).

In many cases the band exists as a doublet, a shoulder appearing at about $10\text{-}m\mu$ longer wavelength than the maximum. The whole absorption moves bathochromically with increasing polarity of the solvent, accompanied generally by a decrease in intensity.

(b) The $n \rightarrow \pi^*$ transition. The general position of this band remains virtually unaltered throughout the series, although there were marked differences in the type of fine structure and the degree of resolution. As in the quinones, little enhancement of absorption occurs, probably for the same reasons.

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(c) The charge-transfer transition. In general, Diels–Alder *endo*-adducts of dienes and *p*-benzoquinone have olefin and ene-1,4-dione chromophores so arranged in space that their π -orbitals can overlap, e.g., (I). Therefore, one can expect electronic transitions from the donor olefin to the electron-accepting enedione system to be possible. This may be observed in the spectrum of the compound as absorption additional to that which would be expected for the sum of the two separate chromophores. Furthermore, as an electron acceptor the ene-1,4-dione system is probably weaker than a *p*-quinone group and, therefore, other things being equal, this new absorption is likely to occur at shorter wavelengths than a similar transition in a corresponding *p*-quinone.

The stereochemistry of the whole system is illustrated by the example of the monocyclopentadiene-*p*-benzoquinone adduct (I). Although the relevant orbitals for interaction seem rather distant from each other, evidence for their (occasional) proximity is

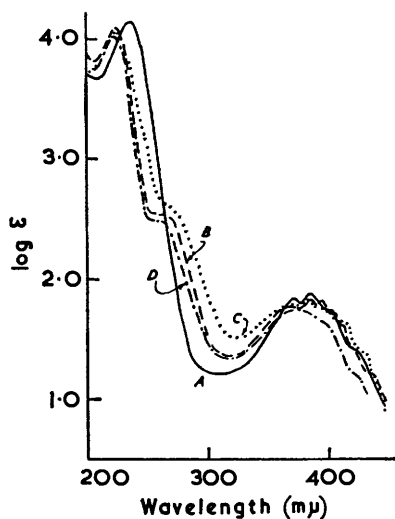


FIG. 3. Ultraviolet spectra of some ene-1,4-diones.

A, (XXXV); B, (XXXI); C, (XXXII); D, (XXXIV) (in cyclohexane).

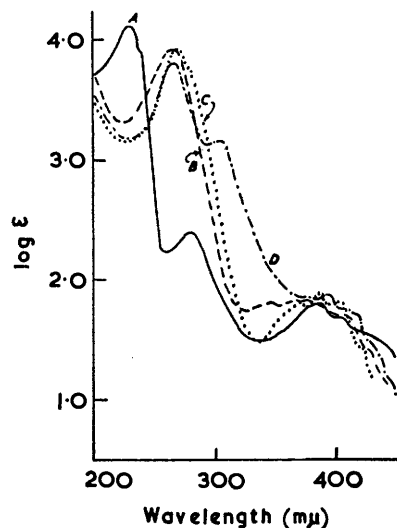


FIG. 4. Ultraviolet spectra of some ene-1,4-diones.

A, (I); B, (XXI) or (XXII); C, (XVIII); D, (XIII) (in cyclohexane).

given by the ease of photoisomerisation to (II).³ In the cyclohexane spectrum of (I) a fairly weak absorption appears as a distinct maximum at 278 $m\mu$. The lowest-energy $\pi \rightarrow \pi^*$ transition is considered to be fully allowed in the enedione system, and therefore responsible for the intense absorption observed in these compounds. Hence, if the new band under discussion is inherent in the chromophore, it would have to be an $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ absorption, both of which possibilities are eliminated by solvent shifts. Therefore, it is suggested that it arises as a result of intramolecular charge-transfer, as discussed above. It is interesting to observe, then, how the intensity and energy of the transition vary as structural changes are made to the basic unit (I) for the process. Firstly, however, let us consider the spectra of the compounds measured which should not show such absorption because of the absence of an interacting olefinic group. (XXXV) exhibits only the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorptions. (XXXVI), however, does show small irregularities in the fall-off of the intense absorption but these were considered too minor to have any connection with the 278 $m\mu$ band of (I). Attempts to synthesise (XXXVII) by partial hydrogenation of (I)³¹ were not completely successful and the

²⁹ Cookson and Dandegaonker, *J.*, 1955, 1651.

³⁰ Crundwell, Ph.D. Thesis, Southampton, 1959.

³¹ Cookson and Hill, *J.*, in the press.

product was never obtained spectroscopically free from the reactant. However, the purest sample available showed only a slight inflection at 278 $m\mu$, where (I) exhibits a distinct maximum. The intense absorption of (XXI) [or (XXII)] has moved to the very region in which we are interested. Nevertheless, if the 278 $m\mu$ band of (I) was caused by some electronic transition of the enedione chromophore, one would expect it to be affected by the changes which cause the $\pi \rightarrow \pi^*$ absorption to move 40 $m\mu$ towards the visible region, and hence it should be observable at least as a shoulder at longer wavelength. However, the only band which occurs other than the one at 264 $m\mu$ is that due to the $n \rightarrow \pi^*$ transition.

In (XVIII), the necessary double bond for interaction has been introduced, and, apart from substituent effects on the enedione chromophore, we have an almost identical system to that in (I). Therefore, the charge-transfer band probably occurs at about the same wavelength. Unfortunately, in this case, it is liable to be hidden beneath the intense absorption, which is also in this region, as in (XXI)—(XXII). Hence, the shoulder at 279 $m\mu$, to which we have assigned an enedione $\pi \rightarrow \pi^*$ origin by analogy with (I), (XXXIV), (XXXVI), and (XXXVIII), may be, in fact, the charge-transfer band. By introducing another bicycloheptene double bond, (XIII) and (XIX), we depart somewhat from the basic system (I). Again, charge-transfer from the more distant olefinic group would have very nearly the same energy as in (I), so if it occurs, its absorption band is probably buried. The absorptions observed at 306 (XIII) and 295 $m\mu$ (XIX) are most likely due to charge-transfer from the nearer double bond, and, because of the decreased distance, are more intense than is generally observed for the other process. Also, the different stereochemistry allows greater mixing of the charge-transfer transition with the local transitions of donor and acceptor chromophores,¹⁷ accounting for the bathochromic shift [cf. (I) or (XVIII)] as well as the increased intensity. Overlap of ground-state orbitals is unlikely in, *e.g.*, (I) or (XVIII) because of resistance to close approach by exchange repulsive forces,^{24b} so mixing of the charge-transfer with the local enedione transition will be insignificant.

The charge-transfer bands of (XIII) and (XIX) occur at slightly shorter wavelength than the corresponding band of the quinone (XXIX). No doubt, the greater electron affinity of the quinone group accounts for this. We may recall here that the charge-transfer absorption of dimethyl bicyclo[2,2,1]heptadiene-2,3-dicarboxylate occurs at 280 $m\mu$ ¹⁷ and recently an analogous absorption for 2,3-dicyanobicyclo[2,2,1]heptadiene has been observed at 291 $m\mu$.³² These values are in line with the expected trend in electron affinity of the acceptor chromophores.

Variation of the system (I) in other ways in the form of compounds (XXXI)—(XXXIV) provides scope for further observation on the charge-transfer band. In the series (I), (XXXI), (XXXIV), the ionisation potential of the olefinic group is progressively increased, and the expected drop in wavelength of the band maximum is observed. The stereochemistry is only slightly altered through the series, although (XXXIV) is less rigid than the other two. In terms of strain on the donor double bond, (XXXII) is intermediate between (I) and (XXXI). It also has the added feature of the cyclobutene double bond, which can be considered capable of participation in the charge-transfer process. Both properties suggest that the donor ionisation potential and therefore the charge-transfer energy should be less than in (XXXI). This is confirmed on measurement of its u.v. spectrum, in which the band is at longer wavelength than in (XXXI) (by about 10 $m\mu$) and is approaching the value for (I). In order to find out whether this was due to strain, cyclobutene participation, or both, the readily available compound (XXXIII)³⁰ was measured. The charge-transfer band of the latter is observed at shorter wavelength than for (XXXII), suggesting that there is some cyclobutene participation in the process (the strain difference between cyclobutene and cyclobutane being assumed to have a

³² Cookson and Dance, *Tetrahedron Letters*, in the press.

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negligible effect on the ionisation potential of the donating double bond. The longer-wavelength absorption must come from the antisymmetric combination of the two donor orbitals.)

Almost all the intramolecular charge-transfer bands of the compounds measured suffer bathochromic solvent shifts.

Again, any ground state interaction between the unsaturated carbonyl system and double bonds in other parts of the molecules is not observed in the C=C and C=O i.r. stretching frequencies. The effects of variation in other structural features must be more important (Table 7).

The possibility of the presence of quinols. The so-called charge-transfer transitions in both enediones and *p*-quinones happen to occur in the same region as the moderately intense absorption of quinols (*i.e.*, 270–320 $m\mu$). Therefore, the possibility of traces of these compounds being responsible must be eliminated. Several relevant quinols were measured and the position of their absorption maxima in the above region is recorded in Table 6, together with the absorption in the same region of the corresponding enediones and *p*-quinones. There is only one case of ambiguity and that is between (XI) and (XIII). This fact in itself is fairly strong evidence against quinols being present in the solutions used for measurements, because, if it were general with the enedione and quinone systems,

TABLE 6.

Comparison of c-t bands with those of related quinols in the same region (in cyclohexane; wavelengths in $m\mu$).

c-t enedione	(I)	(XIII)	(XVIII) ^a	(XXI) ^a or (XXII)	(XXXI)
	278	306	—	—	267
Quinol	(XVIId; R = H)	(XVI; R = H)	(XI)	(XXIX)	(XIt)
	295	297	308	296–303	285–290
c-t quinone	(XVII) ^b	(XIV)	(XII)	(XXIX)	(XIIIt) ^a
	—	307	345	305–320	(XXVIII)
					294
					302

^a Band absent or hidden. ^b Band absent.

TABLE 7.

Infrared spectra of ene-1,4-diones in carbon tetrachloride (frequencies in cm^{-1}).

Compd.	C=O Stretch	C=C enedione	C=C donor	Other absorptions
(I)	1680	1609	1575	1644 ^a
(XXXI)	1682	1617	Hidden	1650 ^a
(XXXII)	1681	1618	Hidden	1650 ^a
(XXXIII)	1684	—	—	
(XXXIV)	1696	1603	1665	
(XXXVIII)	1692	1602	1555	1661 (weak)
(XXXV)	1672	1633		
(XXXVI)	1682	1616		
(XXI) or (XXII) ...	1665	1602	Hidden	1627 (weak)
(XIII)	1663	1603	1564	
Bicyclo[2,2,1]heptene			1569	1617
				1638

^a Point of inflection.

one would expect the maxima to be the same in any set of three (Table 6). However, the ambiguity was removed by refluxing an alcoholic solution of (XIII) for 30 minutes, under nitrogen, recovering the compound, and measuring its spectrum. The identity of the extinction coefficients of the relevant maxima with those of a freshly purified sample eliminated the possibility of quinol formation under such milder conditions as the preparation of a solution in cyclohexane at room temperature.

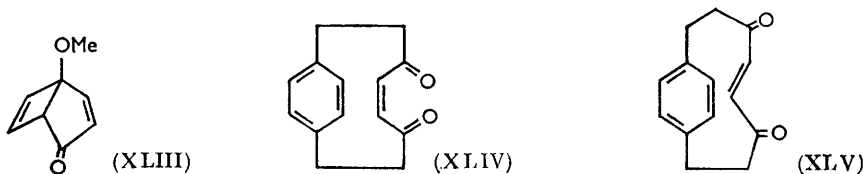
Photochemistry.—The evidence of transannular interaction in the compounds under discussion suggested that their photochemical study might be rewarding. In fact, by the time this work was completed ⁵ the photochemistry of the enediones had already been

investigated³ and the results will be presented in full later. The quinones gave largely polymers when irradiated. The experiments were performed under a variety of conditions, both in solution under nitrogen and in the crystalline state. (XVII) and (XXVIII) were the most photosensitive, losing their colour in solution in a matter of minutes. However, apart from traces of a pale yellow, crystalline, dimeric substance from the irradiation of (XVII) which was not investigated further, no product of interest was isolated. Nevertheless it was interesting to note that the photosensitivity of (XVII) is considerably greater than that of its unsaturated analogue, (XIV), which may be recovered virtually unchanged after several hours of irradiation in 0.01M-ether solution. This difference was also noticed with the two enediones (I) and (XXXVII); (I) photoisomerises to (II) much more slowly than (XXXVII) photodimerises, even below 0.01M.

Other Related Systems.—The cyclopentenone (XLI) is known to photoisomerise to the cage-like compound (XLII) with great ease,³³ so we measured its u.v. spectrum and found an absorption which may be attributed to charge-transfer from the olefinic double-bond to the $\alpha\beta$ -unsaturated ketone chromophore. The full results are given below. In this connection we recall that the photoisomer of γ -tropolone methyl ether (XLIII) has an absorption maximum at 243 m μ in ethanol.³⁴ The negligible enhancement of $n \rightarrow \pi^*$ intensity is to be expected because of poor overlap of the n and donor orbitals, the weak charge-transfer absorption, and the relatively large gap in energy between the two transitions.

Solvent	Cyclopentenone		c-t	$n \rightarrow \pi^*$
	$\pi \rightarrow \pi^*$			
Cyclohexane	λ_{\max} 220.3 m μ (7810)		λ_{sh} 245 m μ (900)	λ_{\max} 342.8 m μ (37)
Ethanol	λ_{\max} 227.0 m μ (7730)		λ_{sh} 257 m μ (720)	λ_{\max} 323.0 m μ (38)

Quite recently, Cram and Knox have prepared two isomers tentatively assigned structures (XLIV) and (XLV) whose spectra are given as follows;³⁵ (XLIV) λ_{\max} 219 (11,560), λ_{sh} 250 (3000), λ_{sh} 310 (480), yellow; (XLV) λ_{\max} 223 (7300), λ_{sh} 249 (3350), λ_{sh} 310 (480), colourless. By analogy with the systems studied here one may correlate



these bands with the following transitions. (i) 219,223 m μ — $\pi \rightarrow \pi^*$ (enedione); (ii) 250,249 m μ —the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ band of benzene, distorted by strain and obtaining some of its intensity from the end absorption of (i); (iii) 310 m μ —charge-transfer from the aromatic ring to the enedione system. Its increased wavelength compared with (I) is likely to be due to the lower ionisation potential of the bent *p*-dialkylbenzene compared with bicycloheptene. The $n \rightarrow \pi^*$ absorptions are probably hidden in the fall-off from (iii), and perhaps it is at longer wavelengths in (XLIV) than (XLV), because the enedione group in the former is forced to adopt the fully cisoid conformation, as shown. The transition responsible for the yellow colour may then come from the high-energy anti-symmetric combination of the overlapping n orbitals of the two oxygen atoms.

EXPERIMENTAL

Melting points are uncorrected. Ultraviolet spectra (in 1-cm. cells for readings above and 0.1 cm.-cells below 220 m μ) were recorded on a Unicam S.P. 700, on loan from the Royal Society, and infrared spectra of Nujol mulls on a Unicam S.P. 100 spectrophotometer.

³³ Cookson, Hudec, and Williams, *Tetrahedron Letters*, 1960, **22**, 28.

³⁴ Chapman and Pasto, *J. Amer. Chem. Soc.*, 1960, **82**, 3646.

³⁵ Cram and Knox, *J. Amer. Chem. Soc.*, 1961, **83**, 2205.

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For u.v. and visible irradiation experiments, 125-w Crompton medium-pressure mercury lamps were used. Irradiation of solutions was achieved by the use of a double-walled vessel, cooled on the outside by a water jacket and containing a central Pyrex or quartz glass "finger" into which the lamp could be inserted. All these experiments were performed under nitrogen. For irradiation of crystalline compounds, the reactant was spread evenly over the base of a Pyrex glass Petrie dish fitted with a lid of the same material. The sample was turned over frequently. The lamp was usually clamped 4—8 in. from the dish.

All quinones and enediones were purified immediately before their spectra were measured. This consisted of chromatography on silica gel, light petroleum (b. p. 40—60°) being used as solvent and eluent, followed by recrystallisations from n-hexane.

The compounds (XVI_d; R = H), (XVII), and (XXXVII) are described in ref. 31, (XXXII), (XXXIII), and (XXXVIII) in ref. 30, and (XXXV) in ref. 41. The synthesis of the enedione derivative of caryophyllene (XXXVI) was carried out after the manner of Barton and Lindsey³⁶ by oxidation of the corresponding 4-hydroxycyclohexan-1-one and cyclohexane-1,4-diol derivatives (kindly supplied by Professor Barton) with chromium trioxide and then dehydrogenation of the corresponding cyclohexanedione with selenium dioxide.

1 α ,4 α ,10 $\alpha\alpha$,5 β ,8 β -8 $\alpha\alpha$ -Hexahydro-1,4:5,8-dimethanoanthracene-9,10-dione (XIII).—Freshly sublimed selenium dioxide (2.5 g.) was dissolved in hot dioxan (500 ml.) and the bis-cyclopentadiene-*p*-benzoquinone adduct (V) (5 g.) added. The mixture was gently refluxed for 3 hr., the solvent was distilled off, and the resulting tar extracted with boiling light petroleum (b. p. 40—60°) (250 ml.). After cooling, the extract was chromatographed on silica gel. By this means, fairly pure dione (XIII) (0.75 g.) (15%) was isolated, m. p. 153°; ν_{\max} . 1658, 1670, 1570, 1315, 1300, 732, and 692 cm.⁻¹ (Found: C, 80.4; H, 5.9. C₁₆H₁₄O₂ requires C, 80.6; H, 5.9%). A variety of conditions and solvents were tried for the above reaction, but the procedure described above gave the best yield of (XIII).

Enolisation of (XIII); 1 α ,4 α ,5 β ,8 β -Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-diol (XI).—The dione (XIII) (100 mg.) in ethanol (3 ml.) was treated with a drop of 2N-sodium hydroxide, whereupon the solution became dark reddish brown. It was kept, with occasional shaking, for 5 min., neutralised with a few drops of dilute hydrochloric acid, and the diol (XI) precipitated by the addition of water (25 ml.). After filtering, drying, and recrystallisation, (XI) underwent gradual charring at 250—300°; ν_{\max} . 3425, 1302, 1242, and 723 cm.⁻¹. The yield from the reaction was almost quantitative. Dilute acid effects no change in (XIII).

Oxidation of (XI); 1 α ,4 α ,5 β ,8 β -Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (XII).—The diol (XI) (100 mg.) in ethanol (5 ml.) was treated with concentrated alcoholic ferric chloride solution (1 ml.), and the mixture kept on a water-bath for 10 min. On slowly removing the solvent, glittering orange needles of the quinone (XII) were deposited. The mother-liquor was decanted off, and the product crystallised from benzene-petroleum (b. p. 60—80°) (65%), m. p. 250° (decomp.); ν_{\max} . 3000, 1641, 1581, 1558, 1318, 755, and 701 cm.⁻¹ (Found: C, 81.2; H, 5.1. C₁₆H₁₂O₂ requires C, 81.3; H, 5.1%). Oxidation was not effected by potassium bromate in acid, potassium permanganate, or air on neutral solutions. Silver oxide gave the quinone (XII) with difficulty.

(a) Irradiation in solution. The quinone (XII) (70 mg.), dissolved in light petroleum (b. p. 40—60°) (250 ml.) was irradiated under nitrogen for 12 hr. The yellow colour became less intense and the solution very cloudy. Evaporation of the solvent and Soxhlet extraction of the residue with petroleum (b. p. 40—60°), gave only unchanged quinone (XII) and a brown polymer. The quinone (XII) (200 mg.) irradiated in ethyl acetate (200 ml.) for 24 hr., gave only the polymer.

(b) Irradiation in the crystalline state. The quinone (XII) (70 mg.), spread evenly over the base of a Petrie dish with a Pyrex lid, was irradiated for 4 weeks and then extracted (Soxhlet) with petroleum (b. p. 40—60°), yielding unchanged quinone (XII) and polymer.

(a) Irradiation of (XIII) in solution. A solution of the enedione (XIII) (200 mg.) in petroleum (b. p. 60—80°) (200 ml.) was irradiated for 6 hr. The solvent was then evaporated off, and the resulting residue extracted with petroleum, from which a 50% yield of the white photoisomer, 1 α (H),5 α (H)-heptacyclo[10,2,1,1^{5,8},0^{2,11},0^{4,9},0^{2,6},0^{7,11}]hexadec-13-ene-3,10-dione (XV), m. p. 153°, was obtained; ν_{\max} . 3060, 1743, 1725, 1570, 735 cm.⁻¹; λ_{\max} . (in EtOH) 310 m μ (ϵ 42) (Found: C, 80.6; H, 6.1. C₁₆H₁₄O₂ requires C, 80.6; H, 5.9%).

³⁶ Barton and Lindsey, *J.*, 1951, 2991.

(b) *Irradiation of (XIII) in the crystalline state.* The enedione (XIII) (200 mg.) was powdered and spread over the base of a Petrie dish and irradiated through a Pyrex glass lid for 20 hr. The solid was then extracted with benzene and petroleum, whereby 60% yield of (XV) was obtained.

Hydrogenation of (XV).—The photoisomer (XV) (120 mg.) in ethyl acetate (100 ml.) was hydrogenated for 3 hr. over 5% palladium-charcoal (30 mg.). The solution was filtered, the solvent removed, and the white residue extracted by and recrystallised from benzene-petroleum to give 1 α (H),5 α (H)-*heptacyclo*[10,2,1,1^{5,8},0^{2,11},0^{4,9},0^{2,6},0^{7,11}]hexadeca-3,10-dione (XVd) (90%), m. p. 140°; ν_{\max} . 1747, 1729, and 1106 cm.⁻¹; ν_{\max} . (in EtOH) 310 m μ , ϵ 32 (Found: C, 79.6; H, 6.7. C₁₆H₁₆O₂ requires C, 80.0; H, 6.7%).

5,8-Diacetoxy-1,4-dihydro-1,4-methanonaphthalene (XVI; R = Ac).—This compound was synthesised from the cyclopentadiene-*p*-benzoquinone monoadduct (25 g.), according to the method of Vaughan and Yoshimine,³⁷ and isolated in 62% yield; it formed white crystals, m. p. 104°.

5,8-Diacetoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene (XVIId; R = Ac).—This compound, m. p. 121°, was obtained in quantitative yield from (XVI; R = Ac) (3.9 g.), according to Meinwald and Wiley's method.³⁸

1 α ,2,3,4 α ,10 α ,5 β ,8 β ,8 α -Octahydro-1,4:5,8-dimethano-anthracene-9,10-dione (XVIII).—The diacetate (1.5 g.) (XVIId; R = Ac) in ethanol (500 ml.) was treated with hydrochloric acid (10%; 100 ml.). The mixture was refluxed under nitrogen for 2 hr. It was concentrated to about 200 ml. and neutralised by the addition of solid sodium hydrogen carbonate and a little water to prevent precipitation of sodium chloride. The mixture was then extracted with ether (5 \times 100 ml.) and the extract allowed to dry (MgSO₄). Some of this solution (25 ml.) was evaporated to a gum which, on extraction with benzene, gave pale pink leaflets of the diol (XVIId; R = H),³¹ m. p. 174–178°.

To the main bulk of the ethereal solution was added silver oxide (5 g.) and anhydrous magnesium sulphate (6 g.), and the mixture shaken for 1 hr., after which it was reduced to a deep orange tar, which according to its i.r. spectrum contained a very high percentage of the quinone (XVII).³¹ Isolation of pure quinone (XVII) was not attempted but the tar was treated in benzene solution with excess of cyclopentadiene, the mixture becoming very warm. It was cooled and kept in a dark cupboard for 2 days. Removal of the solvent and crystallisation gave the required enedione (XVIII) in 60% overall yield [from (I)]. It was a pale yellow crystalline solid, m. p. 133°; ν_{\max} . (Nujol) 1660, 1605, 1575, and 718 cm.⁻¹ (Found: C, 79.9; H, 6.7. C₁₆H₁₆O₂ requires C, 80.0; H, 6.7%).

Irradiation of the enedione (XVIII). The enedione (250 mg.) in ethyl acetate (250 ml.) was irradiated for 12 hr. (under nitrogen). The solvent was removed and the residue extracted with petroleum (b. p. 40–60°) in a Soxhlet extractor. By this means, 40% yield of the cage compound (XVd) was obtained, identical in all respects with that obtained by hydrogenation of (XV).

*Isomerisation of the Biscyclopentadiene-*p*-Benzoquinone Adduct (V) with Alkali.*—(a) *Under nitrogen.* The adduct (V) (1 g.) in ethanol (15 ml.) was refluxed under nitrogen with 15% alcoholic potassium hydroxide (5 ml.) for 30 min. The solution was cooled rapidly and set aside. By removing the alcohol and successive precipitations by the addition of water, and filtrations, the products were obtained as white crystals. These were dissolved in benzene, and the resulting solution dried (MgSO₄). After filtration, petroleum (b. p. 60–80°) was added together with a little more benzene and the total volume of solvent adjusted so that the two solvent components were present in equal quantities and the solute remained in solution. The solution was then passed through a column of silica, the same 1 : 1 solvent mixture being used as eluent. By taking a series of 30-ml. fractions and using i.r. spectra for characterisation, it was possible to separate three crystalline solids. The first was a high-melting compound (15%) [260–270° (decomp.)]; ν_{\max} . (Nujol) 3020, 1710sh, 1701, 1574, 1258, 728, and 720 cm.⁻¹ (Found: C, 80.05; H, 6.6. C₁₆H₁₆O₂ requires C, 80.0; H, 6.7%). The second was the expected isomer, m. p. 184°, 1 α ,4 α ,4 α ,5 β ,8 β ,8 α ,9 α ,10 α -octahydro-1,4:5,8-dimethanoanthracene-9,10-dione (VI), which was obtained in 45% yield; ν_{\max} . (Nujol) 1708, 1575, 1255, 746, and 715 cm.⁻¹; λ_{\max} . (in EtOH) 292 m μ (ϵ 37). The third was the starting material (5%), m. p. 155°; ν_{\max} . 1693, 1655sh, 1574, 1248, 1200, and 712 cm.⁻¹; λ_{\max} . (in EtOH) 300 m μ (ϵ 43). After these compounds

³⁷ Vaughan and Yoshimine, *J. Org. Chem.*, 1957, **22**, 7.

³⁸ Meinwald and Wiley, *J. Amer. Chem. Soc.*, 1958, **80**, 3667.

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had been eluted, solvents of increasing polarity were used in the usual way, but only gums containing hydroxy-groups (i.r.) were obtained.

(b) *Under air.* The same procedure was used as above with 5 g. of (V), except that the nitrogen atmosphere was omitted. Chromatography of the products yielded, besides small quantities of the colourless compounds isolated above, considerable quantities (25%) of the quinone (XII).

Hydrogenation of the Adduct (V).—This reaction was performed according to Alder and Stein's method² with 10 g. of (V). 1 α ,2,3,4 α ,4a β ,5 β ,6,7,8 β ,8a α ,9a β ,10a α -Dodecahydro-1,4:5,8-dimethanoanthracene-9,10-dione (Vt), m. p. 242—245°, was obtained in 88% yield; ν_{\max} . 1680, 1481, 1255, and 1225 cm.⁻¹; λ_{\max} . (in EtOH) 302 m μ (ϵ 33).

Isomerisation of the Dione (Vt) with Alkali.—(Vt) (2 g.) in ethanol (100 ml.) was refluxed for 30 min. under nitrogen with 15% alcoholic potassium hydroxide (10 ml.). The solution was cooled quickly and most of the product precipitated by the addition of water. The aqueous filtrate was extracted overnight with ether, the solution dried, and the solvent removed. The residue was added to the dried precipitate from the filtration and the whole taken up in hot benzene, which solution, on cooling, deposited the desired isomer, 1 α ,2,3,4 α ,4a β ,5 β ,6,7,8 β ,8a β ,9a β ,10a β -dodecahydro-1,4:5,8-dimethanoanthracene-9,10-dione (VIIt). Eventually, a 40% yield of this compound was obtained, which when recrystallised from benzene melted at 220—224°; ν_{\max} . 1700, 1300, and 871 cm.⁻¹; λ_{\max} . (in EtOH) 290—296 m μ (ϵ 40). The yellow mother-liquor from which (VIIt) crystallised, was passed through a column of silica and eluted with benzene. The unknown white crystalline compound (10%), m. p. 266—268°, was eluted first; ν_{\max} . 1753w, 1730, 1715, 1682, 1660w, 1310, 914, and 762 cm.⁻¹; λ_{\max} . (in EtOH) 210 (ϵ 7500) and 305 (56) [Found: (i) C, 70.6; H, 6.0 (O—23.40%) (ii) C, 70.5; H, 5.8 (O—23.7). C₁₆H₁₆O₄ requires C, 70.6; H, 5.9% (O—23.50%)]. The next compound was the quinone (XIIIt) (10%),³⁹ followed by the white crystalline isomer of the starting material 1 α ,2,3,4 α ,4a α ,5 β ,6,7,8 β ,8a β ,9a α ,10a β -dodecahydro-1,4:5,8-dimethanoanthracene-9,10-dione (VIIIt) (18%), m. p. 164°; ν_{\max} . 1693, 1226, and 890 cm.⁻¹; λ_{\max} . (in EtOH) 290—301 m μ (ϵ 56). Finally a 5% yield of the quinol (XIIt) was obtained. The remainder of the product appeared to be a series of alcoholic gums.

Reaction of (Vt) with Methyl-lithium.—The dione (Vt) (100 mg.) in benzene (15 ml.) was treated with excess of methyl-lithium (13 mg.) in ether (80 ml.) under nitrogen. Most of the ether was distilled off, and the mixture refluxed for 3 hr. and set aside at room temperature for 2 days. During the working up process, solid carbon dioxide was added to keep oxygen away from the mixture. Ethanol was added to remove the excess of methyl-lithium, then 50 ml. of water. The aqueous fraction was extracted with benzene, the extract dried (MgSO₄) and then added to the benzene fraction. The resulting solution was chromatographed on silica, whereby the dione (Vt) (30 mg.) and quinone (XIIIt) (20 mg.) were obtained. No other simple product was observed.

Reaction of (VIIt) with Methyl-lithium.—To the dione (VIIt) (500 mg.) in benzene (50 ml.) was slowly added, with stirring, methyl-lithium (44 mg.) in ether (10 ml.). The mixture was refluxed overnight, after which ethanol (30 ml.) was added. The solvent was removed under a vacuum and the resulting gum extracted with hot benzene (300 ml.). The extract was concentrated and chromatographed on silica by which means the quinone (XIIIt) (50 mg.), dione (VIIt) (250 mg.), and enedione (XXI) or (XXII) (30 mg.), were obtained in that order. The enedione, which was slightly impure, had ν_{\max} . 1660 and 1602 cm.⁻¹ (Found: C, 80.1; H, 6.9. C₁₆H₁₆O₂ requires C, 79.3; H, 7.5%).

Similar treatment of the two diones (Vt) and (VIIt) with isopropyl-lithium⁴⁰ also afforded autoxidation products, which included the other enedione (XXII) or (XXI), mentioned in the discussion.

1,4-Dihydro-1,4-methanonaphthalene-5,8-dione (XIV).—This was prepared from the diacetate (XVI; R = Ac) (10 g.) according to Meinwald and Wiley's method.³⁸ The quinone (XIV) (88%) was obtained, m. p. 66°; ν_{\max} . 1645, 1581, 1560, 1313, 841, and 735 cm.⁻¹.

(a) *Irradiation in solution.* The quinone (XIV) (500 mg.) in ether (250 ml.) was irradiated for 3 hr., whereupon a polymer was precipitated. This was filtered off, the solvent removed from the filtrate, and the residue taken up in 1:1 benzene-petroleum (b. p. 60—80°). The solution was chromatographed on silica gel, but gave only unchanged (XIV) and more polymer.

³⁹ Diels and Alder, *Chem. Ber.*, 1929, **62**, 2362.

⁴⁰ Clark, Ph.D. Thesis, Southampton, 1962.

⁴¹ Hudec, to be published.

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(b) *Irradiation in the crystalline state.* The quinone (XIV) (500 mg.) was spread on the base of a Petrie dish, and irradiated, without using a Pyrex lid, by a mercury lamp 1 ft. distant. After 40 hr., the reactant was extracted (Soxhlet) but yielded only the quinone (XIV) and a brown intractable non-crystalline substance.

A duplicate experiment, using a Pyrex lid and working up by extraction and chromatography was likewise unproductive.

Addition of Cyclopentadiene to the Quinone (XIV); $1\alpha, 4\alpha, 10a\beta, 5\alpha, 8\alpha, 8a\beta$ -Hexahydro-1,4:5,8-dimethanoanthracene-9,10-dione.—The quinone (XIV) (1 g.) in benzene (15 ml.) and cyclopentadiene (0.8 g.) were set aside overnight. The solvent was removed and the residue recrystallised from petroleum (b. p. 60–80°). A quantitative yield of enedione very similar to (XIII) was obtained, m. p. 130–138°.

An attempt to separate the product into its components was made by dissolving it in petroleum (b. p. 60–80°) and running the solution on to a large column of silica. Slow elution with benzene gave 14 fractions of enedione which were examined by i.r. spectroscopy. The first and last fractions were recrystallised several times. Eventually, the latter gave a fairly pure sample of a new compound (XIX), m. p. 152–154°, which was not (XIII), but very similar to it; ν_{\max} 1654, 1301, 1286, and 720 cm^{-1} . The other component of the mixture of enediones was (XIII) (i.r. and mixed m. p.). The yields, estimated from i.r. spectra, were (XIX) ~80%, (XIII) ~20%.

Isomerisation and Oxidation of the Enedione (XIX).—The enedione (XIX) (100 mg.), which probably contained a little of the trienedione (XIII), was treated in precisely the same manner as described for the enolisation of (XIII) and oxidation of (XI) (above). It behaved in the same way and similar yields of an analogous quinol and quinone were obtained. The latter melted at 235–245° (decomp.) and had a practically identical i.r. spectrum to (XII).

Irradiation of (XIX): $1\alpha(H), 5\beta(H)$ -Heptacyclo[10,2,1,1^{5,8},0^{2,11},0^{4,9},0^{2,6},0^{7,11}]hexadec-13-ene-3,10-dione.—A conical flask containing the enedione (30 mg.), which probably contained a little (XIII), in petroleum (b. p. 60–80°; 15 ml.) was irradiated (under nitrogen) for 3 hr. The now colourless solution was filtered and concentrated, giving a white photoproduct (40%), m. p. 125–133°; mixed m. p. with (XVd), 120–127°; ν_{\max} 1740, 1720, 1571, 1111, 738, and 664 cm^{-1} .

5,8-Diacetoxy-1,4-dihydro-1,4-ethanonaphthalene (XL) and *1,4-Dihydro-1,4-ethanonaphthalene-5,8-dione* (XXVIII).—The adduct (XXXI) (see below) (800 mg.) in ethanol (15 ml.) was treated with 2*N*-sodium hydroxide (5 drops). After 5 min., the dark solution was neutralised with dilute hydrochloric acid and a small sample withdrawn. This was diluted with water, precipitating some quinol (XL) which after crystallisation from benzene had m. p. 180° (decomp.); ν_{\max} 3300, 1454, 1296, 809, 786, and 730 cm^{-1} . The main part of the neutral solution was poured into water (50 ml.) and the mixture extracted with ether. After partially drying (MgSO_4), the ether extract was treated with silver oxide (2 g.) and anhydrous magnesium sulphate (3 g.). The mixture was shaken for 1 hr., filtered, solvent removed, and the residue taken up in petroleum (b. p. 40–60°). This was chromatographed on silica, from which an 80% yield of the *quinone*, (XXVIII) was obtained, m. p. 96–97°; ν_{\max} 1650, 1582, 1335, and 846 cm^{-1} (Found: C, 77.2; H, 5.8. $\text{C}_{12}\text{H}_{10}\text{O}_2$ requires C, 77.4; H, 5.4%).

1\alpha, 2, 3, 4\alpha, 5\beta, 8\beta-Hexahydro-1,4:5,8-dimethanoanthracene-9,10-dione (XXIX).—The enedione (XVIII) (100 mg.) in ethanol (5 ml.) was treated with 2*N*-sodium hydroxide (2 drops). After 5 min., the solution was neutralised with dilute hydrochloric acid and the quinol precipitated with water. After being filtered and dried, the quinol was taken up in much benzene and treated with silver oxide (0.8 g.) and anhydrous magnesium sulphate (1 g.). The mixture was set aside with occasional shaking for 2 hr. After filtration and concentration, the solution was chromatographed on silica, whereby an 80% yield of (XXIX) was obtained, m. p. 205° (decomp.); ν_{\max} 1646, 1572, 1557, 1325, 752, and 700 cm^{-1} (Found: C, 80.7; H, 5.9. $\text{C}_{16}\text{H}_{14}\text{O}_2$ requires C, 80.6; H, 5.9%).

Irradiation. The quinone (XXIX) (20 mg.) in petroleum (100 ml.) (b. p. 40–60°) was irradiated under nitrogen for 4 hr. Working up as for (XII) yielded only polymer.

1, 2, 3, 4, 9, 9-Hexachloro-1,4-dihydro-1,4-methanonaphthalene-5,8-dione (XXX).—The enedione (XXXVIII) (500 mg.) was dissolved in warm ethanol (15 ml.), and 10% alcohol potassium hydroxide (2 drops) added. After neutralisation with dilute hydrochloric acid, the white quinol was precipitated by addition of water. This was filtered off, dried, and dissolved in the minimum amount of carbon tetrachloride. After the addition of 8 drops of dinitrogen tetroxide,

the mixture was set aside overnight after which the solvent was removed, and the residue dissolved in petroleum (b. p. 60—80°) and a little benzene. This solution was chromatographed on silica gel, by which means the desired quinone (XXX) (300 mg.) was obtained, m. p. 119°; ν_{max} 1661, 1595, 1570, 1292, 1097, 840, and 829 cm^{-1} (Found: C, 35.15; Cl, 56.4. $\text{C}_{11}\text{H}_2\text{Cl}_6\text{O}_2$ requires C, 34.2; Cl, 56.2%).

Irradiation. A solution of the enedione (XXXVIII) (10 mg.) in petroleum (20 ml.) (b. p. 40—60°) was irradiated under nitrogen for 26 hr. The solution went cloudy and developed a nauseating odour. Further examination of its contents revealed only unchanged (XXXVIII) and an intractable gum.

Measurement of Intermolecular Charge-transfer.—As only the positions of the charge-transfer bands were required, a qualitative procedure was adopted as follows: (i) A base-line was run with the solvent (cyclohexane or chloroform) in the sample and reference cells. (ii) To the sample cell was added 1, 2, 4, 8, 16, 32, etc., drops of the donor and to the reference, equal volumes of solvent. This was done to determine the position and nature of the end-absorption of the donor. (iii) Standard solutions of the acceptor were made up in either chloroform or cyclohexane (about 4 mg./ml.) and placed in both sample and reference cells. A base-line was run. (iv) The procedure described under (ii) was repeated and the position of the charge-transfer band recorded.

Pure *p*-benzoquinone was obtained from "Technical Grade" by Soxhlet extraction with petroleum (40—60°) and sublimation (3 times).

Cyclohexene and cyclopentene were purified by shaking them with aqueous ferrous sulphate, washing with water, drying (Na_2SO_4), and distillation.

1 α ,4 α ,4 $\alpha\beta$,8 $\alpha\beta$ -Tetrahydro-1,4-ethanonaphthalene-5,8-dione (XXXI).—This compound was prepared from cyclohexa-1,3-diene (15 g.) and *p*-benzoquinone (6 g.) according to the method of Diels and Alder³⁹ to give a 65% yield of (XXXI), m. p. 97° (from ethanol); ν_{max} 1670 and 1612 cm^{-1} .

4 α ,5,8 α -Tetrahydro-1,4-naphthaquinone (XXXIV).—This compound was prepared from butadiene (4 g.) and *p*-benzoquinone (8 g.), according to the method of Diels and Alder,³⁹ giving a 60% yield of (XXXIV), m. p. 57°.

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