Cookson, Crundwell, Hill, and Hudec:

586. *Photochemical Cyclisation of Diels–Alder Adducts.*

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endo-Adducts of cyclopenta- or cyclohexa-1,3-dienes with cyclohexa-1,4-dienes, especially *p*-benzoquinones (Ia), cyclise on ultraviolet irradiation to cage-like isomers (Ib) by formation of a cyclobutane ring from the two double bonds. The effects of interaction between the two carbonyl groups in the photoisomers (Ib) appear in their infrared and ultraviolet spectra.
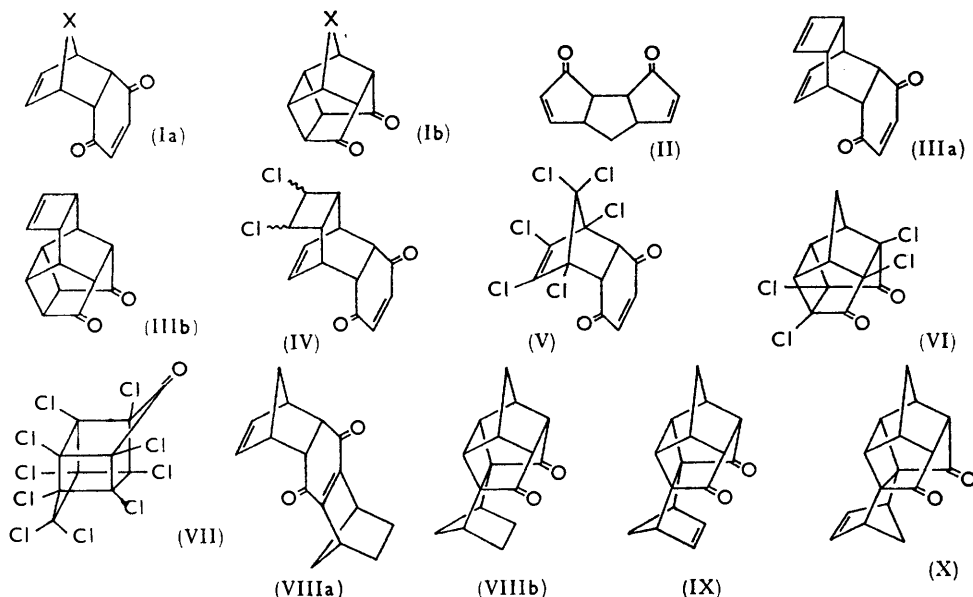
ALTHOUGH the addition of two molecules of a conjugated olefin to form a cyclobutane dimer is one of the oldest and most widely used photochemical reactions,[1] the intramolecular version was represented by only one authenticated example [2] when this work began. However, it seemed likely that if two double bonds were within reach of one another in the same molecule, especially if one of them was conjugated with a chromophore to catch the light, photochemical addition would occur. The possibility of making highly strained structures [2] in this way was attractive.

The 1 : 1 adducts of *p*-benzoquinone and cyclic dienes (Ia) have structures which seemed ideal to meet these requirements. In fact, the cyclopentadiene adduct (Ia; X = CH₂) is converted in high yield into an isomer by ultraviolet irradiation of a light petroleum

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[1] For reviews see Schönberg and Mustafa, *Chem. Rev.*, 1947, **40**, 187; Schönberg, " Praparative Organische Photochemie," Springer Verlag, Berlin, 1958, p. 22.

[2] Cristol and Snell, *J. Amer. Chem. Soc.*, (a) 1954, **76**, 5000; (b) 1958, **80**, 1950. For subsequent examples see Büchi and Goldmann, *ibid.*, 1957, **79**, 4741; Büchi and Burgess, *ibid.*, 1960, **82**, 4333; Chapman and Pasto, *ibid.*, 1960, **82**, 3642.

solution.[3] The isomer was saturated to permanganate and bromine, and incorporated no deuterium when boiled with alkaline deuterium oxide in dioxan. Its saturation (and thus possession of two new rings) was confirmed by its transparency at 210 mμ (ε 230 in ethanol);

the only maximum at longer wavelength was at 287 mμ (ε 24) corresponding to the presence of saturated carbonyl groups. Accordingly, the characteristic infrared absorption of the bicycloheptene double bond ($\nu_{max.}$ 1575 cm.$^{-1}$) and the enedione group ($\nu_{max.}$ 1680, 1644, and 1609 cm.$^{-1}$) in the diene (Ia; X = CH$_2$) had disappeared in the photoisomer, which, furthermore, had no absorption in its proton magnetic resonance spectrum below τ 6·5.

All the properties of the photoisomer are consistent with its being the straightforward cyclobutane isomer (Ib; X = CH$_2$) of the diene (Ia; X = CH$_2$). The high stretching frequency of the carbonyl groups agrees with their situation in strained cyclopentanone rings (see later). Attempts to establish more conclusively that there had been no rearrangement during the isomerisation, by cracking the photoisomer by heat, light, or palladium on charcoal [2a] back to cyclopentadiene and *p*-benzoquinone [or to (II)], failed; under mild heating it sublimed unchanged while at higher temperatures a black tar was formed. However, on one occasion traces of yellow needles, smelling of *p*-benzoquinone, were formed, accompanied by cyclopentadiene. Irradiation with short-wavelength ultraviolet light gave a brown powder with a featureless infrared spectrum.

The reaction * seems fairly general for *endo*-adducts of *p*-benzoquinones with cyclopenta- or cyclohexa-1,3-dienes. Ultraviolet light smoothly converted, into exactly analogous saturated cage isomers, the adducts of benzoquinone with cyclohexadiene {Ia; X = [CH$_2$]$_2$}, cyclo-octatetraene (IIIa) [the photoisomer (IIIb) took up one mole of hydrogen over palladium on charcoal] and its dichloride (IV), and hexachlorocyclopentadiene (V). The adduct of chloranil and cyclopentadiene also gave a photoisomer (VI) which showed an exceptionally high carbonyl stretching frequency (1780 cm.$^{-1}$), in line with that of the perchloro-ketone (VII)(1786 cm.$^{-1}$).[4] We have also observed the
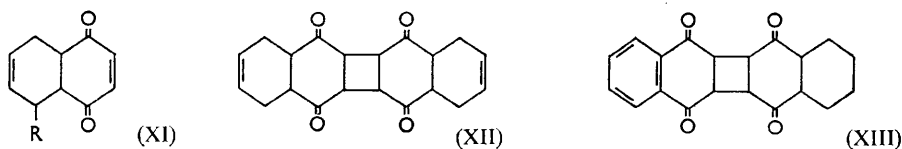
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* After the appearance of our preliminary note [3] we learnt that the photoisomerisation of benzoquinone adducts had been independently observed in the laboratory of Professor C. H. De Puy (Iowa State College, Ames, U.S.A.), who very generously offered to leave the field to us.

[3] Cookson, Crundwell, and Hudec, *Chem. and Ind.*, 1958, 1003.
[4] Earle, Idol, McBee, and Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 1511.

photoisomerisation when the basic structural unit for the process is incorporated into derivatives [5] of the 2 : 1 cyclopentadiene–benzoquinone adduct, *e.g.*, (VIIIa) ⟶ (VIIIb). The diketones (IX) and (X) can be obtained from analogous enediones.

Irradiation of solutions in ethyl acetate of the adduct, (XI; R = H) of butadiene and *p*-benzoquinone, and its derivative (XI; R = CO$_2$H), gave only tars. Diels and Alder [6] had already reported that exposure of crystals of the adduct (XI; R = H) to sunlight yielded a high-melting isomer or polymer. The analytical results were confirmed but the substance was too insoluble for the determination of its molecular weight. Nevertheless, its infrared spectrum ($\nu_{max.}$ 3010, 1710, 1655, 660 cm.$^{-1}$) and the fact that it took up two equivalents of hydrogen over palladium, leave little doubt that it is the dimer (XII). Dehydrogenation over palladium on charcoal, however, did not yield a cyclobutane dimer of naphthaquinone, one isomer of which is known.[7] Although the infrared spectrum of the white, sparingly soluble, product greatly resembled that of the known naphthaquinone dimer (m. p. 244—248°), it did not melt, but slowly decomposed between 240 and 300°. Furthermore, it gave an analysis for the dimer (XII) less *one* molecule of hydrogen, which

suggested internal oxidation–reduction [8] had taken place. If the dimer has a *cis*-configuration about the four-membered ring, then initial oxidation by palladium of one of the cyclohexene rings to a cyclohexadiene could be followed by comparatively easy aromatisation, intramolecularly, whereby the other cyclohexene ring of the molecule is reduced, giving (XIII). Irradiation of (XI; R = CO$_2$H) in the crystalline state produced only tar. With the possibility of alternative photodimerisation in mind, most of the Diels–Alder adducts, which isomerised when irradiated in solution, were irradiated in the crystalline state. However, only isomeric products were detected which were identical to those obtained in solution. Also, in all cases except that of the cyclo-octatetraene adduct (IIIa), the yields were equally high. We may recall here that irradiation of dihydro-(Ia; X = CH$_2$), *i.e.*, in which the bicycloheptene double bond has been reduced, gave a dimer with a structure analogous to (XII).[9]

It appears, then, that even when the molecule has two suitable chromophores which are sterically capable of cyclobutane ring formation, the reaction does not occur unless a bridged ring is involved. No adducts of the form (Ia; X = O), between furans and *p*-benzoquinones, had been reported until Eugster [10] recently announced the isolation of such an adduct between 3,4-dimethoxyfuran and *p*-benzoquinone. If (Ia; X = O) exists in a solution of *p*-benzoquinone in furan, it ought to be possible to trap it as the photoisomer (Ib; X = O) by irradiation. After prolonged irradiation, however, no saturated diketone was detected.

In order to establish whether a suitably activated chromophore could add photochemically to a cyclopropane ring as well as to a double bond, we have synthesised a 1 : 1 adduct (XIV) of 2,5-dimethyl-*p*-benzoquinone and bicyclo[2,2,1]heptadiene. Its structure follows from its physical properties. The ultraviolet spectrum showed clearly a monosubstituted enedione chromophore [5] and the infrared spectrum indicated the presence of

[5] Cookson, Hill, and Hudec, preceding Paper.
[6] Diels and Alder, *Ber.*, 1929, **62**, 2362.
[7] Schönberg, Mustafa, Barakat, Latif, Monbasher, and Mustafa, *J.*, 1948, 2126.
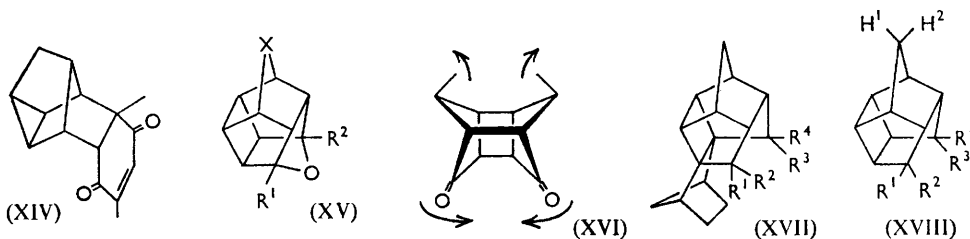[8] Jackman, *Adv. Org. Chem.*, 1960, Vol. 2, 329.
[9] Cookson and Hill, *J.*, 1963, 2023.
[10] Eugster, *Angew. Chem., Internat. Edn.*, 1963, **2**, 50.

the tricyclene moiety.[11] This was further confirmed by the nuclear magnetic resonance spectrum (see Experimental section).

Neither irradiation of the adduct in the crystalline state nor in solution yielded the desired photoproduct with a cyclopentane in place of a cyclobutane ring. Instead, a high-melting white dimer and an oil with acidic properties were obtained.

The cage-like structures of the photoisomers are interesting in that they contain a rigid cyclohexane-1,4-dione ring. This feature also occurs in the 2 : 1 diene–*p*-benzo-quinone adducts and their tetrahydro-derivatives,[5,12] but in the photoisomers the proximity

(XIV)　　　　　　(XV)　　　　　　(XVI)　　　　　(XVII)　　　(XVIII)

of the two carbonyl groups is such that mutual interference is observed in the chemical and spectroscopic properties. Thus, on exposure to air they form insoluble monohydrates which show no carbonyl-stretching frequency in their infrared spectra, and revert to the diketones on heating. Clearly, structures such as (XV; $R^1 = R^2 = OH$) are involved. It was interesting to observe that the ease of formation and corresponding difficulty of dehydration of the hydrates seem to depend on X. Those with two-carbon bridges were formed very readily on exposure of the diketone to air, especially in solution, but temperatures above 150° were needed before they lost water, whereas, for example, (XV; $X = CH_2$, $R^1 = R^2 = OH$) was formed comparatively slowly and was completely dehydrated after being heated for a few hours at 80°. Examination of models revealed that rigidity in the structures of the diketones leads to a certain dependence of the inter-carbonyl distance and angle on the size of X, as shown (XVI). The two-carbon bridge photoisomers having the greater carbonyl π–π repulsion find hydrate formation a more energetically favourable process than the one-carbon bridge diketones, and the carbonyl carbon atoms are more easily spanned by an oxygen atom.

Catalytic hydrogenation of the diketone (IX) over platinum dioxide gave a ketol, and, surprisingly, a diol. The stereochemistry of hydrogenation requires structures (XVII; $R^1 = H$, $R^2 = OH$, $R^3R^4 = O$) and (XVII; $R^1 = R^4 = H$, $R^2 = R^3 = OH$) for these compounds and there is some support for the ketol in the low OH and C=O stretching frequencies (ν_{max} 3320 and 1710 cm.$^{-1}$), presumably due to hydrogen bonding. The corresponding ketol of (Ib; $X = CH_2$), (XVIII; $R^1 = H$, $R^2 = OH$, $R^3R^4 = O$), together with two isomeric diols (m. p. 274 and 276°), was obtained when the diketone was treated with sodium borohydride.[13] In an attempt to methylate the ketol with methyl iodide and silver oxide to give spectroscopically interesting methoxy-ketone (XVIII; $R^1 = H$, $R^2 = OMe$, $R^3R^4 = O$), the ketal (XV; $X = CH_2$, $R^1 = H$, $R^2 = OMe$) was obtained. Of the three possible structures for the diols (XVIII), (*a*) $R^1 = R^4 = H$, $R^2 = R^3 = OH$ (*cis*); (*b*) $R^1 = R^3 = H$, $R^2 = R^4 = OH$ (*trans*); and (*c*) $R^1 = R^4 = OH$, $R^2 = R^3 = H$, the last may be eliminated on the grounds of the stereochemistry of the reduction. The simplicity of the nuclear magnetic resonance spectrum of the diol (m. p. 276°), showing a single resonance corresponding to two tertiary protons at τ 6·24, indicated that this isomer has the symmetrical structure (XVIIIa) and that the diol (m. p. 274°) has the *trans*-configuration (XVIIIb). The *trans*-diol may arise by internal reduction of the second carbonyl group by the hydroborate formed from the first.
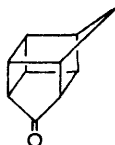
[11] Hanack, *Annalen*, 1961, **648**, 1.
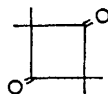[12] Winstein, de Vries, Heck, and Piccolini, *Chem. and Ind.*, 1959, 1416.
[13] Colinese, Ph.D. Thesis, Southampton, 1961.

Further evidence of transannular participation was observed in a number of standard carbonyl addition reactions with the diketones. Thus, treatment of the photoisomer (Ib; $X = CH_2$) with an equimolar quantity of methyl-lithium gave the hemi-ketal (XV; $X = CH_2$, $R^1 = Me$, $R^2 = OH$) in low yield. However, if excess of methyl-lithium was used, the diol (XVIII; $R^1 = R^4 = Me$, $R^2 = R^3 = OH$) was obtained. The configuration follows from the identity of the two methyl groups (nuclear magnetic resonance spectroscopy) and from the stereochemistry of the addition. With hydroxylamine, phenyl-hydrazine, and 2,4-dinitrophenylhydrazine, the same diketone yielded products for which the infrared spectra and analytical data were consistent with structures [XV; $X = CH_2$, $R^1 = R^2 = NHOH,HCl$, $NH \cdot NH \cdot Ph$, and $NH \cdot NH \cdot C_6H_3(NO_2)_2$, respectively].[13]

Ultraviolet Spectra.—The important features of the ultraviolet spectra of the photoisomers are given in Table 1, and a few of the curves in the Figure. A weak absorp-

(XIX)   (XX)

tion is observed between 210 and 230 mμ, which is absent in the spectrum of the strained ketone (XIX)[14] or that of the ketol (XVIII; $R^1 = H$, $R^2 = OH$, $R^3R^4 = O$). One

TABLE 1.

Ultraviolet spectra of photoisomers.

Compound	Solvent	ε at 200 mμ	Features[a] (200—240 mμ (region)	$n \longrightarrow \pi^*$ [a, c]
(Ib; $X = CH_2$) ...	Ch	125	Max. 219(125)	301(27), 318(26)
	EtOH	620	Smooth tail-off	287(24)
{Ib; $X = [CH_2]_2$}	Ch	440	Max. 218·5(144)	303·5(47)
	EtOH	ca. 1000[505][d]	Smooth tail-off	289·5(45)[22·5][d]
Dihydro-(IIIb) ...	Ch	495	Max. 218·5(155)	303(59)
	EtOH	ca. 850[277][d]	Smooth tail-off	289(54)[18][d]
(VIIIb)	Ch	1600	Max. 228·5(436)	303·5—318·5(35)
	EtOH	1640	Shoulder ca. 232(400)	306(40)
(IX)	Ch	3080	Broad shoulder 214—222 (1100—800)	304·5(49), 316(45)
	EtOH	3060	Broad shoulder 213—227 (1100—800)	303(56), 314·5(50)
(X)	Ch	4700	Broad shoulder 218—232 (1050—500)	304(39), 315·5(39)
	EtOH	4300	Broad shoulder 216—232 (1100—800)	304(43)
(XVIII; $R^1 = H$, $R^2 = OH$, $R^3R^4 = O$)	Ch	250	Smooth tail-off	287(6)
	EtOH (95%)	700	Shoulder 202(500)	283(13)
(XIX)[14]	Ch	650	Smooth tail-off	298—303(16)
	EtOH	450	Smooth tail-off	296(14)

[a] Wavelengths in mμ, extinction coefficients given in parentheses. [b] Ch = cyclohexane. [c] Show fine structure, main maxima quoted. [d] Uncorrected values, see text.

concludes, therefore, that it arises from interaction between the two carbonyl groups, which is also implied in the comparison of other features of the spectra throughout the series (see later). The most significant property of the new band is its apparent hypsochromic shift with increasing solvent polarity; in fact in ethanol it disappears into the increased end-absorption. This behaviour, together with its low intensity, is strongly characteristic of $n \longrightarrow \pi^*$ [15] and $n \longrightarrow \sigma^*$ [16] transitions. The ultraviolet spectrum of dimethylketen
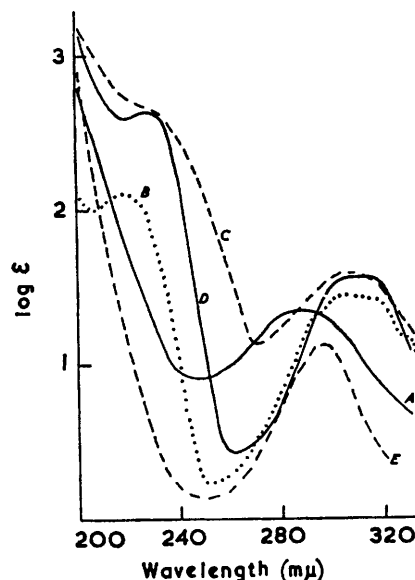
[14] Cookson, Hudec, and Williams, *Tetrahedron Letters*, 1960, No. 22, 28.
[15] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[16] Ito, Huang, and Kosower, *Trans. Faraday Soc.*, 1961, **57**, 1662; Stevenson, *J. Amer. Chem. Soc.*, 1962, **84**, 2849.

dimer (XX) in cyclohexane has been reported recently [17a] as consisting of three weak maxima at 228, 309, and 350 mμ (ε 220, 35, and 17, respectively). Overlap of σ and π systems of the carbonyl groups results in symmetric and antisymmetric combinations giving rise to two $n \longrightarrow \sigma^*$ and two $n \longrightarrow \pi^*$ transitions. The latter may be assigned to the 309 and 350 mμ bands (antisymmetric and symmetric π^* combinations, respectively) leaving the 228 mμ absorption to correspond to the least energetic of the $n \longrightarrow \sigma^*$ transitions, *i.e.*, that involving the symmetric σ^* combination, $n \longrightarrow \sigma_s^*$. The anti-symmetric $n \longrightarrow \sigma^*$ transition, $n \longrightarrow \sigma_a^*$, together with the $\pi \longrightarrow \pi^*$ and $\sigma \longrightarrow \sigma^*$ transitions of the system, occur below 200 mμ. Because of this information, we are inclined to favour an $n \longrightarrow \sigma_s^*$ origin for the 220 mμ band of the photoisomers, despite the fact that the analogy breaks down in there being, apparently, only one $n \longrightarrow \pi^*$ absorption in these compounds.† The position, intensity, and solvent-shift of the absorption is similar in the photoisomers {Ib; X = CH$_2$ or X = [CH$_2$]$_2$} and dihydro-(IIIb), but

Ultraviolet spectra of some polycyclic ketones. *A*, (Ib; X = CH$_2$) in ethanol. *B*, (Ib; X = CH$_2$) in cyclohexane. *C*, (VIIIb) in ethanol. *D*, (VIIIb) in cyclohexane. *E*, (XIX) in cyclohexane.

is observed at 10 mμ longer wavelength and three times as intense in the case of the diketone (VIIIb). It is tentatively suggested that here one is observing the effect of "mixing" between the $n \longrightarrow \sigma_s^*$ transition and a $\sigma_c \longrightarrow \sigma_{c=o(s)}^*$ charge-transfer transition, where σ_c represents a bonding C–C or C–H σ orbital involved in, or strongly influenced by, the bicyclo[2,2,1]heptane residue of the molecule, which is not present in the diketone (Ib; X = CH$_2$) (cf. "mixing" of $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions [17b]). Also, whereas the blue solvent-shift in the case of the diketone (Ib; X = CH$_2$) is at least 8 mμ, there is practically no movement of the band in the compound (VIIIb). It may be argued that in the mixed $n \longrightarrow \sigma_s^*$ transition, the n electron to be excited is located predominantly between the additional bicycloheptane ring and the carbonyl group, and is therefore sterically protected from a hydrogen-bonding solvent.

† Possibly, the better overlap of the oxygen lone-pair orbitals in, say, the photoisomer (Ib; X = CH$_2$) than in the cyclobutanedione (XX) could account for this. If the difference in energy between the two $n \longrightarrow \pi^*$ transitions is reduced as a consequence, the observation of two separate bands may not be possible. In this connection, it is interesting that the shapes of the 300 mμ $n \longrightarrow \pi^*$ absorptions of the one-carbon bridge compounds (Ib; X = CH$_2$) and (VIIIb) are the same, but different from those of the two-carbon bridge compounds {Ib; X = [CH$_2$]$_2$} and dihydro-(IIIb), which are themselves very similar.

[17] (*a*) Mason, *Quart. Rev.*, 1961, **15**, 287. We are indebted to Dr. Mason for drawing our attention to this, and for subsequent discussion; (*b*) Mason, *ibid.*, p. 310.

The 300 mμ absorption of the diketone (Ib; X = CH$_2$) is very nearly twice as intense as that of the strained monoketone (XIX), but differs greatly in solvent-shift (15 and 4 mμ, respectively), implying that some kind of $n \longrightarrow \pi^*$ interaction is present. In the diketones {Ib; X = [CH$_2$]$_2$} and dihydro-(IIIb), the band differs little in position from that of (Ib; X = CH$_2$) but is about twice as intense, probably as a result of a change in the mutual orientation of the two carbonyl groups (XVI). In ethanol, the apparent intensity of this band of the diketone {Ib; X = [CH$_2$]$_2$} is half of the value in cyclohexane. Moreover, in 95% ethanol it drops by a further fifty per cent. Solvate formation is suspected, *e.g.*, as in {XV; X = [CH$_2$]$_2$, R^1 = H, R^2 = OEt}, and, for comparison purposes in other parts of the spectrum, extinction coefficients for pure diketone have been estimated by multiplying the apparent values by the factor needed to bring the $n \longrightarrow \pi^*$ extinction coefficient into line with the value in cyclohexane [by analogy with (Ib; X = CH$_2$), where the $n \longrightarrow \pi^*$ extinction coefficients are similar in the two solvents]. A similar adjustment has been made to the ethanol figures for the other two-carbon bridge diketone, dihydro-(IIIb). The more intense $n \longrightarrow \pi^*$ absorption of (VIIIb) may be understood in terms of " mixing " with a possible $\sigma_c \longrightarrow \pi_{c=o}^*$ transition which would lie below 200 mμ. The observed negligible solvent-shift may then be explained in a similar way to that of its $n \longrightarrow \sigma_s^*$ absorption.

The variation in end-absorption at 200 mμ is, in many ways, consistent with the above assignments. Thus the fact that in ethanol the extinction coefficient at 200 mμ for (Ib; X = CH$_2$) is five times that in cyclohexane is partly due to the generally observed bathochromic shift of $\pi \longrightarrow \pi^*$ and $\sigma \longrightarrow \sigma^*$ bands which occur at shorter wavelength, but also to the hypsochromic shift of the new $n \longrightarrow \sigma_s^*$ transition. The very large value for (VIIIb) in both solvents, compared with (Ib; X = CH$_2$), arises mainly from the $\sigma_c \longrightarrow \pi_{c=o}^*$ and $\sigma_c \longrightarrow \sigma_{c=o(s)}^*$ transitions mentioned above, which probably lie not very far below 200 mμ.

The spectra of the unsaturated diketones (IX) and (X) have been measured, although introduction of an olefinic group necessarily means considerable end-absorption and consequent masking of any low-intensity features at short wavelengths. In addition, one expects the photoisomer (IX) to exhibit a weak absorption at about 220 mμ, due to $\pi_{c=c} \longrightarrow \pi_{c=o}^*$ charge transfer.[18] As expected, the $n \longrightarrow \pi^*$ extinction coefficients for compounds (VIIIb) and (X) are similar, and an increase is observed for compound (IX). Interestingly, the solvent-shift for this band of (IX) is negligible, whilst that of (X) is intermediate between the shifts for (VIIIb) and (Ib; X = CH$_2$).

Following the observation of intramolecular charge transfer from alkoxyl oxygen lone-pair electrons to a carbonyl group,[19] we have examined closely the short-wavelength spectrum of the ketol (XVIII; R^1 = H, R^1 = OH, R^{3}R^4 = O). Only end-absorption is observed in cyclohexane, but in 95% ethanol a definite shoulder appears at 202 mμ. This probably has the same origin as the reported [19] absorption band, for the difference in ionisation potential between hydroxyl and alkoxyl oxygen lone-pair electrons would lead one to predict the higher energy for the transition in the hydroxy-ketone. As already mentioned, attempts to prepare the methoxy-derivative (XVIII; R^1 = H, R^2 = OMe, R^{3}R^4 = O) were unsuccessful.

Infrared Spectra.—As features were observed in the ultraviolet spectra of the cage-like diketones, which suggested interaction between the two carbonyl groups, their C=O stretching frequencies were examined (Table 2). Most cyclopentanones absorb at 1740 $\pm$ 5 cm.$^{-1}$,[20a] and in certain cases, which include cyclopentanone itself, the absorption is split into a doublet due to Fermi resonance.[21] The carbonyl absorption in every one of

[18] Cookson, Hill, and Hudec, *Chem. and Ind.*, 1961, 589.
[19] Yates and Jorgenson, *J. Amer. Chem. Soc.*, 1958, **80**, 6150.
[20] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, (*a*) p. 148, (*b*) p. 128, (*c*) p. 400.
[21] Allen, Ellington, and Meakins, *J.*, 1960, 1909. Yates, Yoda, Brown, and Mann, *J. Amer. Chem. Soc.*, 1958, **80**, 202.

the photoisomers is split into at least two components. In addition to Fermi resonance, mechanical coupling, which is observed in many dicarbonyl compounds, *e.g.*, anhydrides and peroxides,[20b] is possible in the photoisomers because of the rigidity of the structures. Comparison of the frequency differences, $\Delta\nu$, between the two main components of the absorptions for the two-carbon bridge diketones {Ib; X = $[CH_2]_2$, (IIIb), and dihydro-

TABLE 2.

C=O stretching frequencies of photoisomers (frequencies in cm.[-1]).

Compound	(Ib; X = CH₂)	{Ib; X = [CH₂]₂}	(IIIb)	Dihydro-(IIIb)	(VIIIb)	(IX)	(X)	(XIX)	Cyclo-pentanone
ν_{max} (CHCl₃) [a]	*1758*	*1788*	*1760*	*1757*	*1744*	*1749*	*1747*	*1757*	
	1749	*1759*	1738	1737	1727	1732	1730	1745	
	1739	1741	1711						
	1705	1719							
ν_{max} (CCl₄) [a] ...	*1763*	*1765*	*1766*	*1765*	*1749*	*1754*	*1754*	*1762*	*1747*
	1750	1753	1740	1743	*1735*	*1742*	*1740*	1745	1731
	1739								
	1729								
$\Delta\nu$(CCl₄) [b] ...	13	12	26	22	14	12	14	17	16
$\bar{\nu}$(CCl₄) [b]	1757	1759	1753	1754	1742	1748	1747	1754	1739

[a] Main maximum in italics. [b] $\Delta\nu$ = frequency difference between two main maxima; $\bar{\nu}$ = mean of the frequencies of the two main maxima.
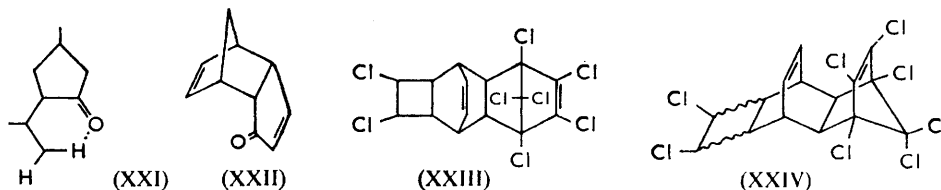
(IIIb) indicates Fermi resonance as being the most important factor, for here rigidity and the mutual disposition of the two carbonyl groups are practically identical in all three molecules, and yet a considerable change in $\Delta\nu$ is observed when a structural alteration, remote from the absorbing system, is made.

As far as carbonyl–carbonyl interaction is concerned, one would really like to know the C=O stretching frequencies, unperturbed by the above effects. Unfortunately, the mean of the two main maxima can only be taken for this value when they are of the same intensity, and this is not always so. Consequently, small shifts within the series must be ignored. Nevertheless, it is evident that these compounds have very high stretching frequencies compared with other cyclopentanones. The figures for the monoketone (XIX) indicate that the largest fraction of this increase comes from angle strain. However, comparison with the considerably less strained diketone {Ib; X = $[CH_2]_2$} clearly suggests that a dipolar-field effect [20c] is present in the latter and therefore in all the diketones. The difference between the values for the compounds (Ib; X = CH_2) and {Ib; X = $[CH_2]_2$}, although small and therefore of doubtful significance, is consistent with the difference in intercarbonyl angle (XVI), as the strength of the dipolar field increases as this decreases. The large shift to lower frequencies when (Ib; X = CH_2) carries a bicycloheptane residue, as in photoisomer (VIIIb) (15 cm.[-1]), or a bicycloheptene residue, as in photoisomers (IX) and (X) (10 cm.[-1]), is somewhat unexpected. The introduction of further strain on the cyclobutane ring of photoisomer (Ib; X = CH_2) could conceivably increase either the cyclopentanone −C−CO−C− bond angle or the intercarbonyl angle, or both, all of which would give rise to a lower C=O stretching frequency. The lower value for the diketone (VIIIb), compared with those of its unsaturated analogues (IX) and (X), may be due to hydrogen bonding (XXI),[22] for, although the hydrogen atom is not particularly acidic, a sterically favourable position for such bonding is enforced by the rigidity of the structure.

Nuclear Magnetic Resonance Spectra.—The spectra of most of the cage-like compounds are rather complex. In most cases, the predominant feature is a rather broad absorption, corresponding to the tertiary protons, which is sometimes split into two groups. The other feature common to all of these structures is a resonance due to methylene protons which, in the diol (XVIII); $R^1 = R^4 = H$, $R^2 = R^3 = OH$), have different chemical shifts, showing doublets centred at τ 8·96 and 8·37, with a coupling constant of 10·5 c.p.s. In the diketone (Ib; X = CH_2), this difference is reduced by the unshielding effect of the carbonyl

[22] Sutor, *J.*, 1963, 1105.

groups, and the absorption consists of two doublets centred at τ 8·17 and 7·91, thus implying that the lower-field doublet corresponds to H[1] (XVIII). Comparison of the spectra generally reveals that the protons in the polycyclic compounds experience a complex magnetic field, presumably produced by ring currents, etc., in the carbon skeleton. For reference, the chemical shifts of the main peaks in the spectra are given in the Experimental section.

Nature of the Photoisomerisation.—The mechanism of the reaction is of particular interest in view of the presence of a charge-transfer absorption in the ultraviolet spectrum [5] of (Ia),† which, in simple terms, involves excitation of an electron in the highest filled molecular orbital of the bicycloheptene double bond to the lowest vacant molecular orbital of the enedione chromophore. It seemed likely that this was the first step towards complete bonding between the two groups, as exists in the products (Ib). However, irradiation of (Ia; X = CH$_2$) using a salicylaldehyde filter of path-length 1 cm. (which cuts out all light of wavelength shorter than 415 mμ) yielded a small amount of (Ib; X = CH$_2$). This practically eliminates direct participation of a charge-transfer process, for one would expect the corresponding absorption to have negligible intensity at 415 mμ, and " mixing " with the $n \longrightarrow \pi^*$ transition is also eliminated as the two transition moments are orthogonal (except when coupled with a twisting vibration). Unless one considers possible the participation of a (forbidden) singlet–triplet version of the 278 mμ band which might well occur near 400 mμ, the photoisomerisation must result from the $n \longrightarrow \pi^*$ absorption of the enedione system.

The heats of isomerisation, ΔH_i, were obtained for three systems by measuring the

TABLE 3.*

Heats of isomerisation ΔH_i for three systems.

Compound	Heat of combustion $-\Delta H_c$	Heat of formation ΔH_f	Average heat of formation	Heat of isomerisation ΔH_i
(Ia; X = CH$_2$) ...	1. 1340·82 2. 1339·11 3. 1340·32	−35·34 −37·05 −35·83	−36·07	For (i) (Ia) $\longrightarrow$ (Ib; X = CH$_2$) $\Delta H_i = -11·32$
(Ib; X = CH$_2$) ...	1. 1329·77 2. 1329·67 3. 1326·87	−46·39 −46·48 −49·29	−47·39	
{Ia; X = [CH$_2$]$_2$}	1. 1484·24 2. 1486·66	−54·28 −51·86	−53·07	For (ii) (Ia) $\longrightarrow$ {Ib; X = [CH$_2$]$_2$} $\Delta H_i = -4·23$
{Ib; X = [CH$_2$]$_2$}	1. 1482·32 2. 1480·76 3. 1480·73 4. 1481·37	−56·20 −57·76 −57·80 −57·16	−57·23	
(XXII)	1. 1277·749 2. 1278·449 3. 1278·6801	−4·354 −3·654 −3·423	−3·810	For (iii) (XXII) $\longrightarrow$ (XIX) $\Delta H_i = +16·41$
(XIX)	1. 1294·4824 2. 1294·0641 3. 1295·552	+12·379 +11·961 +13·449	+12·596	

* Values given in kcal./mole.

† In cyclohexane, the ultraviolet spectrum of (Ia; X = CH$_2$) consists of three maxima: 226 mμ (ε 12,900), 238 mμ (ε 6800sh), enedione $\pi \longrightarrow \pi^*$; 278 m$\mu$ (ε 250), charge-transfer $\pi \longrightarrow \pi^*$; 385 m$\mu$ (ε 58), $n \longrightarrow \pi^*$.

heats of combustion of the reactants and products (Table 3).* In contrast to the dimerisation of cinnamic to truxillic acids, where little gain or loss of energy is involved,[23] reaction (i) is considerably exothermic, presumably because of the release of strain from the bicyclo[2,2,1]heptene system. In accord with this is the lower negative heat of isomerisation in the bicyclo[2,2,2]octene case, (ii). The cage-like structure (XIX) embodies more than enough strain to compensate for the energy lost by saturation of the bicycloheptene system [in (XXII)], and the net reaction [(iii)] is endothermic. The difference between ΔH_i for (Ia; $X = CH_2$) and {Ia; $X = [CH_2]_2$} is *ca.* 7 kcal./mole which is of the same order as the difference between the heats of hydrogenation of bicyclo[2,2,1]heptene and bicyclo[2,2,2]octene (*ca.* 5 kcal./mole).[24]

The photoisomerisations discussed so far depend on the enedione chromophore to absorb the energy. However, we have also observed similar photoisomerisations in chloro-derivatives of certain polycyclic hydrocarbons.[25] 1,2,3,4,7,7-hexachlorobicyclo[2,2,1]hepta-diene adds to 7,8-dichlorobicyclo[4,2,0]octa-2,4-diene to give two 1 : 1 adducts, m. p. 245—246 and 164—165°. Irradiation of each isomer gave a saturated photoisomer, m. p. 270 and 218°, respectively, which lacked the C=C stretching absorption of the adducts (1600 cm.$^{-1}$) and had low absorption (ε 250) at 210 mμ. Hence, of the four possible Diels–Alder adducts (XXIII) (excluding the different configurations possible for the chlorine atoms on the cyclobutane ring), the two photoisomers produced must be the pair with the double bonds adjacent (XXIV), differing only in the configuration of the cyclobutane ring-junction.

EXPERIMENTAL

Ultraviolet spectra were measured on a Unicam S.P. 700 spectrophotometer using 1-cm. cells above, and 0·1-cm. cells below, 220 mμ. The measurement of low extinction coefficients at short wavelengths calls for very pure materials and reliable instrumentation. The samples were purified by means of two or three sublimations and measured immediately. Using ethanol solutions in 0·1-cm. cells, the slit-width of the instrument was *ca.* 0·2 mm. at 200 mμ. Optical densities were measured by reference to a base-line obtained with solvent in sample and reference cells. Each spectrum was measured twice using different batches of purified material, and reproducibility of extinction coefficients within 5% was obtained.

Infrared spectra were measured on a Unicam S.P. 100 spectrophotometer. In obtaining the values given in Table 2, the calibration of the instrument was checked after every measurement, and the results are correct to ±1 cm.$^{-1}$.

N.m.r. spectra of chloroform or carbon tetrachloride solutions were measured on a Varian A-60 machine, with tetramethylsilane (T.M.S.) as internal reference.

Heats of combustion were measured at the Explosives Research and Development Establishment, Waltham Abbey, Essex.

The method used in the ultraviolet and visible irradiation experiments has already been described.[5]

Pentacyclo[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane-3,6-dione* (Ib; $X = CH_2$).—(*a*) *In solution.* The 1 : 1 adduct of cyclopentadiene and *p*-benzoquinone [26] (Ia; $X = CH_2$) (19 g.) in ethyl acetate (300 ml.) was irradiated for 6 hr. The almost colourless solution was evaporated under reduced pressure and the *product* (90%) which crystallised was filtered off, washed, and sublimed (120°/14 mm.), then having m. p. 245°; $\nu_{max.}$ (CHCl$_3$) 1758, 1120, and 1070 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl$_3$) τ 7 (broad absorption) and 8·2 (centre of AB quartet), corresponding to 8 and 2 protons, respectively (Found: C, 76·0; H, 5·8. C$_{11}$H$_{10}$O$_2$ requires C, 75·8; H, 5·8%).

(*b*) *In the crystalline state.* The adduct (500 mg.) was irradiated for 80 hr. and the product (80%) extracted (Soxhlet) with light petroleum (b. p. 40—60°); it had m. p. 245°.

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* These are heats of combustion of the crystalline solids. The differences in heats of sublimation between isomers are unlikely to be large enough to affect the comparisons significantly.

[23] "Chemistry of Carbon Compounds," Ed. Rodd, Elsevier, London, 1956, Vol. IIIB, p. 998.
[24] Turner, Meador, and Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4116.
[25] Bird, Cookson, and Crundwell, *J.*, 1961, 1809.
[26] Diels, Blom, and Koll, *Annalen*, 1925, **443**, 247.

(c) *Hydrate.* Examination of photoisomer (Ib; X = CH_2) which had been exposed to air for 18 months showed it to be partially converted into a hydrate $\nu_{max.}$ (Nujol) 3330, 1418, 1140, and 955 cm.$^{-1}$. The diketone was recovered from the hydrate by heating at 80° for 5 hr., mixing with charcoal, and extracting (Soxhlet) with light petroleum (b. p. 40—60°). During normal chemical manipulations of solutions of the photoisomer, no tendency to form the hydrate was observed, cf. {Ib; X = $[CH_2]_2$} and dihydro-(IIIb), below. The structure of the hydrate is assumed to be (XV; X = CH_2, R^1 = R^2 = OH), by analogy with hydrates of other photo-isomers whose structures have been proved (below).

Pentacyclo[6,2,2,0^{2,7},0^{4,10},0^{5,9}]*dodecane-3,6-dione* {Ib; X = $[CH_2]_2$}.—(a) *In solution.* The 1 : 1 adduct of cyclohexa-1,3-diene and *p*-benzoquinone [6] (1 g.) in ethyl acetate (250 ml.) was irradiated for 10 hr., after which a white deposit began to collect on the walls of the apparatus. Evaporation of the solvent gave a brown, non-crystalline residue from which the product was extracted (Soxhlet) with light petroleum (b. p. 40—60°). Crystallisation from the above solvent gave white *crystals* (80%), m. p. 256°; $\nu_{max.}$ (CHCl₃) 1758, 1240, 1050 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl₃) τ 7·0, 7·5, 7·9 (broad absorptions), and 8·19, corresponding to 4, 2, 2, and 4 protons, respectively (Found: C, 76·0; H, 6·55. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

(b) *In the crystalline state.* The adduct (1 g.) was irradiated for 90 hr. in a Pyrex Petrie dish (with lid) which was frequently turned over. A 90% yield of the photoisomer was obtained after recrystallisation from light petroleum (b. p. 40—60°).

(c) *Hydrate.* Diketone {Ib; X = $[CH_2]_2$} which had been left in air for 18 months was found to be completely hydrated. Concentrated solutions of the diketone in many organic solvents deposited crystals of the hydrate after exposure to air for a few days. The diketone could be recovered by sublimation of the hydrate (170—180°/10 mm.). The *hydrate*, recrystall-ised from ethyl acetate, had $\nu_{max.}$ (Nujol) 3380, 3200, 1310, 1150, 870 cm.$^{-1}$ (Found: C, 69·9; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

2α(*H*),12α(*H*)-*Hexacyclo*[6,4,2,0^{2,7},0^{4,14},0^{5,13},0^{9,12}]*tetradec-10-ene-3,6-dione*, (IIIb).—(a) *In solution.* The 1 : 1 adduct of *p*-benzoquinone and cyclo-octatetraene [27] (10 g.) in ethyl acetate (250 ml.) was irradiated for 2½ hr. Evaporation of the solvent and extraction (Soxhlet) of the residue with light petroleum (b. p. 60—80°) afforded the *photoisomer* (9 g.), m. p. 195—196°; $\nu_{max.}$ (CHCl₃) 3115, 1760, 1738, 1055, (Nujol) 760 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl₃) τ 3·75 (sharp), 6·9, 7·1, 7·5, and 7·7 (broad), corresponding to 2, 4, 2, and 2 protons, respectively (Found: C, 78·6; H, 5·4. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%).

(b) *In the crystalline state.* The adduct (500 mg.) was irradiated through Pyrex glass for 80 hr. Extraction with light petroleum (b. p. 60—80°) afforded the photoisomer (80 mg.), leaving a brown powder as residue.

(c) *Hydrate.* After 18 months' exposure to air, the diketone (IIIb) was found to be almost completely hydrated. Although the hydrate was not examined, it seems certain that its formation is strictly analogous to that of dihydro-(IIIb) (below).

2α(*H*),12α(*H*)-*Hexacyclo*[6,4,2,0^{2,7},0^{4,14},0^{5,13},0^{9,12}]*tetradecane-3,6-dione*; dihydro-(IIIb).— Photoisomer (IIIb) (500 mg.) in ethyl acetate (100 ml.) was hydrogenated, at room temperature and atmospheric pressure, over 5% palladium on charcoal (200 mg.) for 2 hr. After the theoretical amount for one equivalent of hydrogen had been taken up, filtration followed by evaporation of the solvent afforded pure white crystals of dihydro-(IIIb) (450 mg.). After recrystallisation from benzene–light petroleum (b. p. 60—80°), the *product* had m. p. 202—204°; $\nu_{max.}$ (CHCl₃) 1757, 1737, 1048 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl₃) τ 6·55, 7·0, 7·3, 7·6, and 7·9 (broad absorptions) corresponding to 2, 2, 2, 4, and 4 protons, respectively (Found: C, 78·3; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%).

Hydrate. After 18 months' exposure to air, the diketone was found to be almost completely hydrated. The *hydrate*, recrystallised from ethyl acetate, showed $\nu_{max.}$ (Nujol) 3350, 3200, 1315, 1150, 885 cm.$^{-1}$ (Found: C, 72·6; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

10,11-Dichloro-2α(H),12α(H)-hexacyclo[6,4,2,0^{2,7},0^{4,14},0^{5,13},0^{9,12}]*tetradecane-3,6-dione*.—The adduct of 7,8-dichlorobicyclo[4,2,0]octa-2,4-diene and *p*-benzoquinone [28] (IV) (1 g.) in ethyl acetate (50 ml.) was irradiated for 9 hr. with periodic addition of solid carbon dioxide. A white solid (0·7 g.) precipitated which crystallised from tetrahydrofuran to give *flakes* (0·35 g.,

[27] Butz, *Org. Reactions*, 1949, **6**, 168.
[28] Reppe, Schlichting, Klager, and Toepel, *Annalen*, 1948, **560**, 1.

35%), m. p. *ca.* 298° (decomp.); $\nu_{max.}$ (Nujol) 1760 cm.$^{-1}$ (Found: C, 58·5; H, 4·3; Cl, 24·8. $C_{14}H_{12}Cl_2O_2$ requires C, 59·4; H, 4·2; Cl, 25·1%).

1,8,9,10,11,11-*Hexachloropentacyclo*[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*-3,6-*dione.*—The adduct of hexachlorocyclopentadiene and *p*-benzoquinone[29] (V) (5 g.) in ethyl acetate (125 ml.) was irradiated for 85 hr. with periodic addition of small pieces of solid carbon dioxide. The solvent was removed *in vacuo* and the residue extracted (Soxhlet) with light petroleum (b. p. 60—80°). The solid obtained was sublimed (120—140°/*ca.* 10^{-3} mm.) and then crystallised from light petroleum (b. p. 100—120°) to give *flakes* (1·8 g., 36%), m. p. 300° (decomp.); $\nu_{max.}$ (CHCl$_3$) 1760 cm.$^{-1}$ (Found: C, 34·7; H, 1·2; Cl, 55·2. $C_{11}H_4Cl_6O_2$ requires C, 34·65; H, 1·05; Cl, 55·9%).

2,4,5,7-*Tetrachloropentacyclo*[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*-3,6-*dione* (VI).—The adduct of chloranil and cyclopentadiene[30] (2 g.) in ethyl acetate (50 ml.) was irradiated for 4 days with periodic addition of solid carbon dioxide. The solvent was removed *in vacuo* and the residue sublimed (150°/10^{-3} mm.) to give crystals which recrystallised from light petroleum (b. p. 100—120°) as *needles* (1·08 g., 54%), m. p. 215° (decomp.); $\nu_{max.}$ (Nujol) 1780 cm.$^{-1}$ (Found: C, 41·2; H, 2·5. $C_{11}H_6Cl_4O_2$ requires C, 42·4; H, 1·9%).

Dehydrogenation of 1,4,5,7,8,10,11,14,15,17,18,20-*Dodecahydro*-6,9,16,19-*tetraoxo*-2,3′-*di-naphthylene* (XII).—The above compound (20 mg.) in ethyl acetate (15 ml.) was refluxed with 30% palladium on charcoal (50 mg.) for 10 hr. The residue, obtained on removal of the solvent, was extracted (Soxhlet) with ethyl acetate. Evaporation of the yellow extract gave a pale yellow residue which, when washed with a little acetone, afforded a white microcrystalline solid, decomp. >240°, mixed m. p. with authentic naphthaquinone dimer [m. p. 244—248° (decomp.)], 242—250° (decomp.). The *solid* showed $\nu_{max.}$ (Nujol) 1710, 1693, 1682, 1600, 1308, 1272, 1095, 956, 780, 740, and 705 cm.$^{-1}$ (cf. authentic naphthaquinone dimer, $\nu_{max.}$ 1693, 1600, 1273, 1095, 950, 780, and 705 cm.$^{-1}$) (Found: C, 73·9; H, 5·5. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

Addition of 2,5-*Dimethyl-p-benzoquinone to Bicyclo*[2,2,1]*heptadiene.*—2,5-Dimethyl-*p*-benzoquinone (5 g.) was heated in bicyclo[2,2,1]heptadiene (40 ml.) at 80° for 7 days. The reaction mixture was diluted with benzene and chromatographed in the same solvent on silica gel. Elution with benzene gave the starting quinone, and further elution with 9 : 1 benzene–ethyl acetate gave a yellow oil which afforded *crystals* (5—15%), m. p. 133—135° (from ether); $\nu_{max.}$ (CHCl$_3$) 1672 and 1633 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 240 mμ (ε 13,500) and 374 mμ (ε 77); and n.m.r. chemical shifts from T.M.S. (in CCl$_4$) τ 3·45, 7·21, 7·45, 7·8, 8·00, 8·49, 8·74, and 9·15, corresponding to 1, 1, 1, **2, 3**, 2, 4, and 2 hydrogens, respectively (Found: C, 78·9; H, 7·1. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%). Irradiation of the adduct in the crystalline state gave a high melting point non-volatile solid [$\nu_{max.}$ (Nujol) 1710 cm.$^{-1}$]. In ethyl acetate or cyclohexane solution, acidic oils were the sole products.

Hydrogenation of the Diketone (IX) *over Platinum Dioxide.*—The diketone (180 mg.) in ethyl acetate (150 ml.) was hydrogenated for 4 hr. over PtO$_2$ (500 mg.). 50 ml. of hydrogen (atmospheric pressure) were taken up. The solution was filtered and the solvent removed to give a white solid which was extracted and recrystallised from benzene. Two products were obtained: 3-hydroxy-1α(H),3β(H),5α(H)-heptacyclo[10,2,1,1,^{5,8},0^{2,11},0^{2,6},0^{4,9},0^{7,11}]hexadecan-10-one (XVII; R^1 = H, R^2 = OH, R^{3}R^4 = O) (70 mg.) and the corresponding 1α(H), 3β(H), 5α(H),-10β(H)-hexadecane-3,10-diol (XVII; R^1 = R^4 = H, R^2 = R^3 = OH) (15 mg.). The *ketol* had m. p. 152—155°; $\nu_{max.}$ (Nujol) 3320, 1710, 1105 cm.$^{-1}$ (Found: C, 79·1; H, 7·5. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%) and the *diol* m. p. 161—162°; $\nu_{max.}$ (Nujol) 3260, 1117, and 1077cm.$^{-1}$ (Found: C, 78·5; H, 8·2. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·3).

Sodium Borohydride Reduction of the Photoisomer, (Ib; X = CH$_2$).—(*a*) *Using one molar proportion of reductant.* Sodium borohydride (0·095 g., 2·5 mmole) was added to a solution of the photoisomer (1·63 g., 10 mmole) in 95% ethanol (20 ml.). After 10 min., water (5 ml.) was added and the mixture refluxed gently for 10 min. on the steam-bath. More water (35 ml.) was added, and the solution extracted with ether, which was then dried and evaporated. The colourless residue obtained was taken up in benzene and chromatographed on silica. Elution with 9 : 1 benzene–ethyl acetate gave traces of the starting material; 9 : 1 and 3 : 1 benzene–ethyl acetate gave 3-*hydroxy*-1α(*H*),3β(*H*)-*pentacyclo*[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecan*-6-*one* (XVIII; R^1 = H, R^2 = OH, R^{3}R^4 = O) (1·15 g.), which crystallised from benzene as small irregular

[29] Prill, *J. Amer. Chem. Soc.,* 1947, **69**, 62.
[30] Albrecht, *Annalen,* 1906, **348**, 31.

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prisms, m. p. 270—271°; $\nu_{max.}$ (Nujol) 3350, 1740, 1350, 1110, 1080, 1010 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl$_3$) τ 5·4, 6·0, 7·3 (broad absorptions), and τ 8·3 (centre of AB quartet), corresponding to 1, 1, 8, and 2 protons, respectively (Found: C, 74·7; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%). Elution with ethyl acetate gave 3α,6β-*dihydroxypentacyclo*[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*, (XVIII; R^1 = R^3 = H, R^2 = R^4 = OH) (70 mg.), m. p. 273—273·5° (from ethyl acetate–light petroleum); $\nu_{max.}$ (Nujol) 3270, 1350, 1105, 1075, 1050, and 965 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl$_3$) τ 6·1, 7·4, 7·7, and 8·4 (broad absorptions), corresponding to 2, 4, 4, and 2 protons, respectively (Found: C, 74·2; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%).

(b) *Using excess of reductant.* Sodium borohydride (0·38 g., 10 mmole) was added to a solution of the diketone (0·82 g., 5 mmole) in 95% ethanol (15 ml.). After 24 hr. at room temperature, more sodium borohydride (0·38 g.) [in ethanol (15 ml.)] was added. The reaction mixture was worked up as before, but using chloroform as the extractant. Elution with 1 : 1 benzene–ethyl acetate gave 1α(H),3β,6β-*dihydroxypentacyclo*[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*, (XVIII; R^1 = R^4 = H, R^2 = R^3 = OH) (0·3 g.), which crystallised from ethyl acetate as hard plates, m. p. 276—276·5°; $\nu_{max.}$ (Nujol) 1080, 1100, 1275, 1290, and 3270 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CHCl$_3$) τ 3·45, 6·24, 7·42, 7·70, and 8·68 (centre of AB quartet), corresponding to 2, 2, 4, 4, and 2 protons, respectively (Found: C, 74·2; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%). Continued elution with ethyl acetate gave the diol (XVIII; R^1 = R^3 = H, R^2 = R^4 = OH) (0·5 g.).

Methylation of the Ketol (XVIII; R^1 = H, R^2 = OH, R^{3}R^4 = O); 3-*Methoxy-3,6-alkoxy-pentacyclo*[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*, (XV; X = CH$_2$, R^1 = H, R^2 = OMe).—The ketol (160 mg.) in methanol (8 ml.) was treated with methyl iodide (1 ml.) and silver oxide (500 mg.). On gentle warming, the solution became opaque and silver iodide was precipitated. The solution was allowed to stand, with occasional shaking, for 2 days. The methanol was then removed and benzene (several ml.) added. After being dried (MgSO$_4$), the solution was chromatographed on silica gel; this gave, in order of elution, the *product*, (XV; X = CH$_2$, R^1 = H, R^2 = OMe) (100 mg.), a sweet smelling colourless oil, and unchanged ketol (30 mg.). The product showed $\nu_{max.}$ (CCl$_4$) 1341 and 1016 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CCl$_4$) τ 5·54, 6·70, 7·40 (broad absorptions), and τ 8·3 (centre of AB quartet), corresponding to 1, 3, 8, and 2 protons, respectively (Found: C, 75·7; H, 7·2. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

Treatment of the Diketone (Ib; X = CH$_2$) *with Methyl-lithium.*—(a) *Slight excess of methyl-lithium.* Methyl-lithium (16 mmoles) in ether (20 ml.) was added to the diketone (1·7 g.) in ether (80 ml.) and the mixture refluxed with stirring for 6 hr. When the mixture was cool, a little ethanol was slowly added, to destroy any unchanged methyl-lithium present, and the whole was well washed with water. The aqueous and ethereal fractions were worked up separately. The ethereal fraction was dried (Na$_2$SO$_4$) and the solvent evaporated. Extraction of the resulting gum with light petroleum (b. p. 60—80°) and keeping of the extract for several days, eventually produced colourless crystals of 3,6-*epoxy-6-hydroxy-3-methylpentacyclo*-[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*, (XV; X = CH$_2$, R^1 = OH, R^2 = Me) (200 mg.), m. p. 98°; $\nu_{max.}$ (CCl$_4$) 3250, 1355, 1300, 1145, 1010 cm.$^{-1}$; n.m.r. chemical shifts from T.M.S. (in CCl$_4$) τ 7·4, 8·3 (centre of an AB quartet), and 8·6, corresponding to 8, 2, and 3 protons, respectively (Found: C, 75·5; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

The aqueous fraction was extracted with ethyl acetate, and the extract dried (MgSO$_4$). Evaporation of the solvent left a vitreous tar which was extracted with light petroleum (b. p. 60—80°). From the extracts, some of the hemiketal (20 mg.) was isolated, together with unchanged diketone (800 mg.).

(b) *Large excess of methyl-lithium.* To the diketone (1·5 g.) in ether (200 ml.), was added, with stirring, a large excess of methyl-lithium in absolute ether. A vigorous reaction ensued and when this had subsided, the mixture was refluxed for 5 hr. Ethanol was then cautiously added to remove the excess of methyl-lithium, and the whole was well washed with water. As before, the aqueous and ethereal fractions were worked up separately. The aqueous fraction was treated in the same way as above, but the light petroleum extract yielded only a gum with a camphor-like odour, $\nu_{max.}$ 3300, 1195, and 1180 cm.$^{-1}$, which was not investigated further. The ethereal fraction was dried (MgSO$_4$) and the solvent removed, leaving a gum. A little benzene was added, the mixture warmed, and a little light petroleum (b. p. 60—80°) added. On cooling, white feathery crystals of 3α,6α-*dihydroxy*-3β,6β-*dimethyl*-1α(H)*pentacyclo*-[6,2,1,0^{2,7},0^{4,10},0^{5,9}]*undecane*, (XVIII; R^1 = R^4 = Me, R^2 = R^3 = OH) (600 mg.), were

deposited, m. p. 112—114°; $\nu_{max.}$ (CHCl$_3$) 3250 and 1170 cm.$^{-1}$; n.m.r. ·chemical shifts from T.M.S. (in CHCl$_3$) τ 3·3, 7·55, 7·9, 8·7 (centre of AB quartet), and 8·85 corresponding to 2, 6, 2, 2, and 6 protons, respectively (Found: C, 75·6; H, 8·7. C$_{13}$H$_{18}$O$_2$ requires C, 75·7; H, 8·8%).

Treatment of the Diketone (Ib; X = CH$_2$) *with Hydroxylamine Hydrochloride.*—Hydroxyl-amine hydrochloride (0·07 g., 1 mmole) and 1N-sodium hydroxide solution (1 ml.) were added to a solution of the diketone (0·16 g., 1 mmole) in ethanol (10 ml.). The mixture was refluxed for 1 hr., cooled, and filtered. The resulting solid was crystallised from aqueous ethanol to give fine white *crystals* (0·3 g.), m. p. 50°; $\nu_{max.}$ (Nujol) 690, 875, 905, 930, 950, 1100, 1140, 1240, 1285, 3170, and 3270 cm.$^{-1}$ (Found: C, 45·2; H, 4·4; N, 9·3. C$_{11}$H$_{16}$Cl$_2$N$_2$O$_3$ requires C, 45·0; H, 5·4; N, 9·5%).

Treatment of the Diketone (Ib; X = CH$_2$) *with Phenylhydrazine.* Phenylhydrazine (0·09 g., 1 mmole) and the diketone (0·16 g., 1 mmole) were heated together over a small flame for 5 min. The mixture was cooled and crystallised from aqueous ethanol to give a white crystalline *product* (0·35 g.), m. p. 110—112°; $\nu_{max.}$ (Nujol) 700, 750, 1270, 1510, and 1610 cm.$^{-1}$ (Found: C, 74·3; H, 6·4; N, 16·1. C$_{23}$H$_{24}$N$_4$O requires C, 73·8; H, 6·95; N, 15·0%).

Treatment of the Diketone (Ib; X = CH$_2$) *with 2,4-Dinitrophenylhydrazine.*—The diketone (0·16 g., 1 mmole) in ethanol (5 ml.) was added to a solution of 2,4-dinitrophenylhydrazine in ethanol (4 ml.) containing 2 drops of concentrated hydrochloric acid. The mixture was kept for 2 hr., then filtered, and the orange *product* (0·4 g.) crystallised from aqueous ethanol; it had m. p. 159—161° $\nu_{max.}$ (Nujol) 745, 840, 1080, 1150, 1320, 1345, 1430, 1525, 1600, and 1630 cm.$^{-1}$ (Found: C, 51·7; H, 3·7; N, 19·8. C$_{23}$H$_{20}$O$_9$N$_8$ requires C, 50·0; H, 3·6; N, 20·3%).

Irradiation of (Ia; X = CH$_2$) *with Filtered Light.*—A solution of the diketone (20 mg.) in cyclohexane (2 ml.), in a 1-cm. silica cell, was irradiated for 4 days, with light from a 125 w medium-pressure mercury lamp, the light being condensed through a moderately efficient monochromator set at 4358 Å and then passed through a 1-cm. silica cell containing salicyl-aldehyde. Evaporation of the solvent and crystallisation of the residue from light petroleum gave a white solid whose infrared spectrum was identical to that of (Ib; X = CH$_2$).

Adducts of 7,8-*Dichlorobicyclo*[4,2,0]*octa-2,4-diene and* 1,2,3,4,7,7-*Hexachlorobicyclo*[2,2,1] *heptadiene:* 1α(Cl), 2β(H), 3β(H)-1,5,6,10,11,12,13,13-*Octachloropentacyclo*[8,2,2^{3,8},1,0,^{2,9},0^{4,7}]-*pentadec*-14-*ene*, (XXIV).—The octadiene (1·4 ml., 0·01 mole) and the heptadiene (2·25 ml., 0·01 mole) were kept together in a bath at 160° for 20 hr. The tarry product was chromato-graphed on alumina in 2 : 1 benzene–light petroleum to give an oil which, on trituration with light petroleum, gave a white solid (2·16 g.) which crystallised from ethanol as flakes, m. p. 230—235°, and from ethyl acetate as plates (0·3 g., 6%), m. p. 245—246°; $\nu_{max.}$ (CHCl$_3$) 1615 cm.$^{-1}$ (Found: C, 37·4; H, 2·1; Cl, 58·6. C$_{15}$H$_{10}$Cl$_8$ requires C, 38·0; H, 2·1; Cl, 59·9%). Concentration of the ethanol solution gave cubes, m. p. 160—165°, which recrystallised from light petroleum (b. p. 60—80°) as *cubes* (0·32 g., 6%), m. p. 164—165°; $\nu_{max.}$ 1615 cm.$^{-1}$; ε (200 mμ) = 8000 (Found: C, 38·0; H, 2·2; Cl, 57·9. C$_{15}$H$_{10}$Cl$_8$ requires C, 38·0; H, 2·1; Cl, 59·9%).

Photoisomerisations. The higher-melting adduct (0·2 g.) in ethyl acetate (50 ml.) was irradiated in a quartz tube, under an atmosphere of carbon dioxide, for 9 days. The solvent was removed *in vacuo* on a steam-bath and the residue was refluxed for 30 min. with potassium permanganate (0·3 g.) in acetone. The mixture was cooled, filtered, diluted with 4N-sulphuric acid, and extracted with ether which was then dried (Na$_2$SO$_4$). Removal of the ether gave a solid which was chromatographed on alumina in benzene to give a white solid which crystallised from ethanol as *cubes* (0·056 g., 28%), m. p. 269—270°; no max. around 1600 cm.$^{-1}$; ε (210 mμ) = 240 (Found: C, 38·1; H, 2·4. C$_{15}$H$_{10}$Cl$_8$ requires C, 38·0; H, 2·1%). The lower-melting adduct was similarly treated to give *rods* (25%), m. p. 217—218°; no max. around 1600 cm.$^{-1}$; ε (210 mμ) = 460 (Found: C, 38·2; H, 2·5).

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