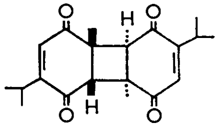
886. *Photodimers of Alkylbenzoquinones.*

By R. C. Cookson, D. A. Cox, and J. Hudec.

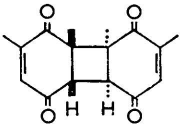
In sunlight the dimethylbenzoquinones dimerise by addition of the double bonds of two molecules to form a cyclobutane ring. The *trans*-dimers are stable to further irradiation, but the *cis*-dimers cyclise through a second reaction of the same sort, forming saturated, box-shaped molecules. All the dimers dissociate to the original monomers on pyrolysis.

The photodimer of thymoquinone has been known for over a century.[1] Its chemical[2] and spectroscopic[3] properties show that it is formed by the coupling of two monomer molecules to form a cyclobutane ring, and the frequency and lack of splitting of the methyl proton resonance[3] show that both methyl groups are attached to quaternary carbon atoms in the dimer: but there is no evidence on whether the monomer units are joined head-to-head or head-to-tail (as in I) or whether the two *cis*-fused cyclohexenedione rings are joined to the same side or to opposite sides of the cyclobutane ring (as in I).

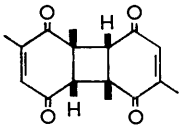
Irradiation of *p*-benzoquinone or its mono-, tri-, or tetra-methyl derivative in solution or as the crystal with light from a medium-pressure mercury arc or from the sun produced no dimer: an insoluble, unsublimable polymer, containing hydroxyl groups, was slowly formed in all cases, accompanied by the corresponding quinol when the solvent had available hydrogen atoms. The three dimethylbenzoquinones, however, yielded a variety of dimers.



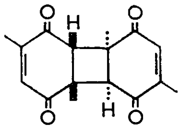
(I)



(II)



(III)



(IV)

Irradiation of crystalline 2,6-dimethylbenzoquinone with sunlight gave variable results until it was realised that the main product, which was rapidly formed, was very unstable to heat: by avoiding exposure to heat during purification a yellow dimer was isolated in high yield. The dimer, which slowly dissociated back to the monomer in solution or even in the crystalline state at room temperature, showed the characteristic bis-enedione chromophore ($\lambda_{max.}$ 246 mμ, ε 22,800; $\nu_{max.}$ 1677 and 1640 cm.$^{-1}$). Its stability to further irradiation with sunlight or a mercury arc, when *cis*-dimers undergo a second cyclisation[4] (see below), suggests that this dimer has a *trans*-configuration.* The extraordinary instability to heat compared with the behaviour of compounds that can differ from it only in the position of methyl groups must be of steric origin. The unstable isomer must then be (II),† strained because of the two linked quaternary centres.

Irradiation of 2,6-dimethylbenzoquinone through Pyrex glass with a mercury arc gave none of the compound (II), but instead two other dimers; these were also produced (in higher yield) with sunlight. One, which was adsorbed rather more strongly on silica gel than the unstable dimer (II), was also yellow, the other was colourless, sparingly soluble, and very high-melting. Structure (VII) will be established for the colourless dimer when it is considered below, with the dimers of the same kind from the other two dimethylbenzoquinones. The second yellow dimer also showed the bis-enedione chromophore

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* In the rest of this paper we use *cis* to denote dimers with both enedione groups on the same side of the cyclobutane ring, and *trans* for those with the enedione groups on opposite sides, assuming that individual ring-fusions are invariably *cis*.

† All the compounds described here are racemic, formulæ showing only one form.

[1] Lallemand, *Ann. Chim. Phys.*, 1857, **49**, 167.

[2] Smith and Tess, *J. Amer. Chem. Soc.*, 1944, **66**, 1323, who give earlier references.

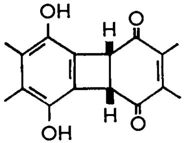
[3] Zavarin, *J. Org. Chem.*, 1958, **23**, 47.

[4] See also Cookson, Crundwell, and Hudec, *Chem. and Ind.*, 1958, 1003.

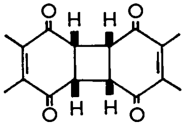
($\lambda_{max.}$ 237 mμ, ε 15,000; $\nu_{max.}$ 1685, 1662, and 1630 cm.$^{-1}$), but in sharp contrast with the unstable dimer (II) it did not decompose at 200°. Further irradiation of this dimer induced fast and quantitative cyclisation to the saturated dimer (VII). Since 2,6-dimethylbenzoquinone itself under the same conditions gave the saturated dimer (VII) more slowly and in much lower yield, the change cannot involve dissociation and recombination. The dimer, therefore, has the *cis*-configuration. Its being merely the *cis*-isomer of the unstable dimer (II) would hardly explain the far slower dissociation. It must then be the alternative *cis*-dimer (III), free from the source of strain present in (II).

Sunlight converted crystalline 2,5-dimethylbenzoquinone in fairly good yield into a mixture of two dimers, one yellow, the other colourless. Under a mercury lamp the colourless isomer only was formed, and in poor yield. On the other hand, ultraviolet irradiation of a solution of the quinone in ethyl acetate gave some of the yellow isomer. Above its m. p. (164°) this yellow dimer dissociated to the monomer. Its stability to further irradiation in the crystal or in solution suggests that it has the *trans*-configuration, and its thermal stability compared with that of dimer (II) showed that the methyl groups on the cyclobutane ring are 1,3-, not 1,2-. It therefore probably has the structure (IV).[5]

Fieser and Ardao,[6] during their work on the quinone antibiotic from the arachnid Gonyleptide, noticed incidentally that sunlight bleached 2,3-dimethylbenzoquinone to a white, insoluble polymer. We found that exposure of the crystalline quinone to sunlight soon gave a mixture of a yellow and a colourless dimer, the proportion of the latter increasing with the time of exposure. The same products were formed more slowly, less cleanly, and in lower yield when a mercury arc was used. Further exposure of the yellow dimer ($\lambda_{max.}$ 248 mμ, ε 17,600; $\nu_{max.}$ 1677 and 1607 cm.$^{-1}$) to light from the sun or the arc gave a quantitative yield of the colourless one [shown below to have structure (IX)]. Since the colourless dimer was formed more rapidly and smoothly from the yellow dimer than from the monomer, the yellow dimer must have the *cis*-configuration. That it had at least two hydrogen atoms on the cyclobutane ring followed from its enolisation to the quinol (V), which gave a diacetate. Comparison of the infrared spectrum of the dimer in the range 1200—1500 cm.$^{-1}$ with spectra of model compounds indicated that it was too simple to come from a molecule containing tertiary methyl groups: in fact the spectrum was very similar to that of monomeric 2,3-dimethylbenzoquinone (see Table). The resulting structure (VI) was clinched by the proton magnetic resonance spectrum (kindly measured by Dr. L. Pratt) which had two sharp peaks at $\tau = 6{\cdot}10$ and $8{\cdot}12$ in the ratio 1 : 3. We are now trying to convert the quinol (V) and the dimer (VI) into derivatives of cyclobutadiene.



(V)



(VI)

Since the dimer of thymoquinone is relatively stable to heat and does not yield a saturated isomer on further irradiation it probably has the *trans*-structure with 1,3-methyl groups (I).

The structures of the three colourless dimers still have to be considered. All were high-melting (or decomposing), sparingly soluble solids that sublimed *in vacuo*, and were clearly all of the same structural type. Their general structure follows from these facts: (1) They are saturated to the usual chemical tests, and show only low end-absorption in the ultraviolet region. (2) They each have a strong band in the infrared spectrum between 1700 and 1715 cm.$^{-1}$. (3) The *cis*-dimers (III) and (VI) form the respective colourless

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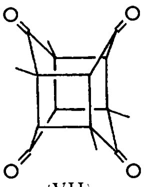
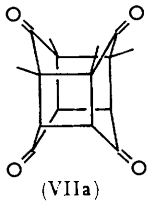
[5] Cookson and Hudec, *Proc. Chem. Soc.*, 1959, 11.

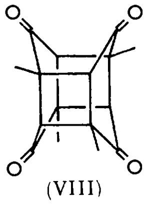
[6] Fieser and Ardao, *J. Amer. Chem. Soc.*, 1956, **78**, 774.

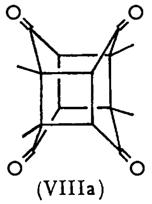
dimers on irradiation, and appear to be intermediates in their formation from the quinones. (4) Each dissociates to its own monomer on pyrolysis. (5) Although the sublimed dimers are anhydrous and contain no hydroxyl groups, they crystallise from solvents such as ethyl acetate as dihydrates which betray by their infrared spectra the presence of hydrogen-bonded hydroxyl groups (3270 cm.$^{-1}$), C–O bonds (1035 cm.$^{-1}$), and lower-frequency carbonyl groups (1690—1700 cm.$^{-1}$). These properties can be explained only by their formation from two molecules of quinone combining at both double bonds, without rearrangement.

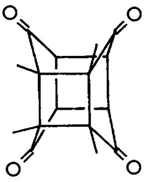
Each dimethylquinone could give two such saturated dimers. If the one from 2,6-dimethylquinone is really formed from compound (III) it must have structure (VII). Pyrolysis of the dimer in the gas phase at 450° gave pure 2,6-dimethylquinone; the infrared spectrum of the total product was identical with that of an authentic sample. Gas chromatography also showed only 2,6-dimethylquinone, although synthetic mixtures of 2,6-dimethylquinone containing small proportions of benzoquinone and duroquinone were well separated. However, this cannot be taken as additional evidence in favour of structure (VII) rather than the alternative (VIIa) because the latter might well cleave almost entirely in the vertical plane, rather than horizontally, because of repulsion between the methyl groups * (cf. the much greater speed of cleavage of II than of III, IV, or VI).

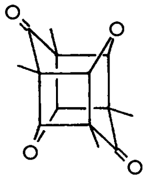

(VII)


(VIIa)


(VIII)


(VIIIa)


(IX)


(X)

Pyrolysis of the colourless dimer from 2,5-dimethylquinone also gave entirely the parent quinone, with no detectable trace of 2,3-dimethylquinone, but again a compound (VIIIa) might split preferentially in the horizontal plane, so that the evidence is not decisive in favour of (VIII). Since no intermediate *cis*-dimer could be isolated in this case, the structure of the colourless dimer must be left in doubt. (In fact it could be argued that the failure to isolate the " half-shut " *cis*-dimer tends to favour VIIIa.)

Pyrolysis of the colourless isomer from 2,3-dimethylquinone gave only the parent quinone, free from any detectable trace of 2,5-isomer. Again, this in itself does not quite exclude (VIIIa), but the synthesis of the dimer from compound (VI) is sufficient proof of structure (IX).

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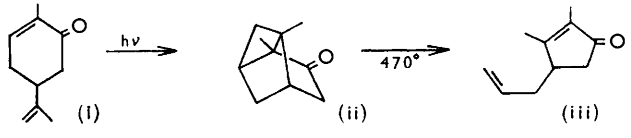
* This expectation is justified only by the symmetry of the ring system in (VIIa): it does not imply that cyclobutanes in bridged-ring structures will always split between quaternary centres. If it releases greater angle-strain, the alternative cleavage may take place—for example,[7] carvonecamphor (ii) gives the cyclopentenone (iii) instead of carvone (i).

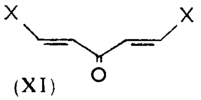


Büchi and Goldman, *J. Amer. Chem. Soc.*, 1957, **79**, 4741.

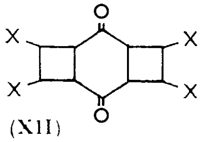
Very recently there appeared a contradictory account[8] of the photodimerisation of 2,3-dimethylbenzoquinone. It was reported, as we have found, to be converted by sunlight into a yellow dimer that on further irradiation gave a colourless one. Except that the carbonyl band of the yellow dimer is rather higher in frequency than that of ours, the properties of the two pairs of isomers make it possible that they are the same. Yet the colourless dimer was said to give 2,5-dimethylbenzoquinone on pyrolysis, requiring structure (VIIIa). If the product of pyrolysis was correctly identified, there seem to be only two likely explanations for the discrepancy: (1) we have used different crystal forms of 2,3-dimethylbenzoquinone, leading to different dimers, or (2) the pyrolysis was carried out under conditions that rearrange 2,3-dimethylbenzoquinone to the 2,5-isomer. We could detect no 2,5-dimethylbenzoquinone when the 2,3-isomer or its dimer was heated in the gas phase or in a sealed tube at temperatures from 300° to 700°.

The photo-dimer of 2,6-dimethyl-4-pyrone has recently been shown[9] to have an analogous structure (X).

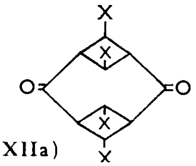
Dimethyl 4-oxohepta-2,5-dienedioate (XI) is converted by sunlight into a saturated dimer[10] for which Stobbe and Färber suggested the structure (XII). They did not consider the alternative (XIIA), which could also arise by formation of two cyclobutane rings. In an attempt to distinguish between the two possibilities, either of which would be consistent with the ultraviolet and infrared spectra, we pyrolysed the dimer.* Dimethyl fumarate was easily isolated but, although the pyrolysate had the characteristic pungent smell, benzoquinone could not be identified and the infrared spectrum of the total product showed that it could not have been present in more than traces. Nevertheless the formation of dimethyl fumarate decides in favour of Stobbe and Färber's structure (XII), and the proton magnetic resonance spectrum is reported to be consistent with this structure.[11] Irradiation of a solution of benzoquinone in dimethyl fumarate gave a product with an infrared spectrum very similar to that of the dimer (XII). Incidentally it was noticed that irradiation of dimethyl fumarate led to tetramethyl *cis-trans-cis*-cyclobutanetetracarboxylate in good yield, as mentioned later by Griffin, Basinski, and Vellturo.[12] All attempts to



(XI)



(XII)



(XIIa)

X = CO_2Me

Infrared maxima (cm.$^{-1}$) for mulls in tetrachloroethylene.

BQ = 1,4-Benzoquinone. A = 2-Methyl-3-phenylcholest-2-ene. B = 3-Methylcholest-2-ene.

2,3-Me_2 BQ	(VI)	2,6-Me_2 BQ	(III)	2,5-Me_2 BQ	(IV)	Thymoquinone	(I)	A	B
1243	1290	1292	1290	1300	1330 *	1310	1295	1302	1323 *
1305	1305	1317	1320 *	1355	1350	1358	1335	1330	1330
1358	1335	1363	1350	1383	1368	1385 *	1360	1345	1345
1375	1370	1383	1378	1438 *	1380	1390	1370	1364 *	1365 *
1435	1435	1435 *	1405	1447	1385 *	1435	1380	1377	1380
		1442	1432		1433	1450	1445	1440	1445
			1456			1470	1458	1465	1465

* Shoulder.

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* We are indebted to Dr. R. G. Lingard for these experiments.

[8] Flaig, Salfeld, and Llanos, *Angew. Chem.*, 1960, **72**, 110.

[9] Yates and Jorgensen, *J. Amer. Chem. Soc.*, 1958, **80**, 6150.

[10] Straus, *Ber.*, 1904, **37**, 3293; Stobbe and Färber, *Ber.*, 1925, **58**, 1548; Midorikawa, *Bull. Chem. Soc. Japan*, 1953, **26**, 302.

[11] Corse, Finkle, and Lundin, *Tetrahedron Letters*, 1961, No. 1, 1.

[12] Griffin, Basinski, and Vellturo, *Tetrahedron Letters*, 1960, No. 3, 13; see also Criegee and Höver, *Chem. Ber.*, 1960, **93**, 2521.

convert the central ring of the dimer (XII) into the quinone or a derivative of the quinone failed.

EXPERIMENTAL

Ultraviolet spectra of ethanol solutions were recorded on a Unicam S.P. 700 and infrared spectra of Nujol mulls on a Unicam S.P. 100 spectrophotometer.

The compounds were irradiated at room temperature through Pyrex glass with a 125-w medium-pressure mercury arc or with sunlight. A thin deposit of crystals for irradiation was obtained by evaporating a solution of the sample in ether on the inside of a relatively large flask.

The various quinones were prepared by standard methods. Toluquinone was prepared from its quinol by oxidation with sodium dichromate in dilute sulphuric acid. Duroquinone was obtained from durene through the dinitro- and diamino-intermediates, according to Smith's method.[13] Trimethylbenzoquinone and the three dimethylbenzoquinones were prepared by oxidation of the corresponding phenols with Fremy's salt.[14]

Toluquinone.—The quinone gradually became brown on irradiation by a mercury lamp or by the sun. After 3 days the product was shaken with a small quantity of ether, and the insoluble brown solid was filtered off. The quinone obtained on evaporation of the filtrate was again irradiated. The solid, accumulated from several such cycles, did not crystallise, but was precipitated from ether by addition of light petroleum (b. p. 40—60°). It began to decompose at about 300°. It did not sublime under a vacuum. The ill-defined infrared spectrum showed peaks due to hydroxyl groups at 1200 and 3400 cm.$^{-1}$, and a max. at 1655 with shoulders at 1740 and 1620 cm.$^{-1}$.

Duroquinone.—The similar, pale brown product from duroquinone was insoluble in all the usual organic solvents. It began to decompose at about 300°, without producing duroquinone. The rather diffuse infrared spectrum again showed the presence of hydroxyl groups: $\nu_{\text{max.}}$ 3350, 1725, 1680, 1645sh cm.$^{-1}$.

Trimethyl-1,4-*benzoquinone.*—Melting of the quinone (32°) was prevented by a finger cooled with ice and salt inserted into the dry nitrogen-filled flask on the inside of which the crystals of quinone had been deposited. After 1½ days' exposure during intermittent sunlight the product was dissolved in ether. Addition of a small amount of light petroleum (b. p. 40—60°) precipitated a white substance: the unchanged quinone was then recycled. The product, which could not be sublimed, melted with decomposition at about 160° and had $\nu_{\text{max.}}$ 3400, 1700, and 1620sh cm.$^{-1}$.

Irradiation of 2,5-*Dimethylbenzoquinone.*—After 4—8 hours' exposure to sunlight the colour of the crystalline quinone had faded considerably. The product was digested with boiling ether and the white substance (A) filtered off. The residue obtained on evaporation of the filtrate was chromatographed in benzene on silica gel. Unchanged quinone, m. p. 125°, was eluted with benzene. Benzene containing 10% of ethyl acetate eluted the *trans*-dimer (IV), 1α,2β,7β,8α-1,4,7,10-*tetramethyltricyclo*[6,4,0,0^{2,7}]*dodeca*-4,10-*diene*-3,6,9,12-*tetraone* [1,4,4a,4bβ,5,8,8a,8bβ-*octahydro*-2,4aα,6,8aβ-*tetramethyl*-1,4,5,8-*tetraoxobiphenylene*], which crystallised from ether in pale yellow needles, m. p. 163—164° (Found: C, 70·8; H, 5·9. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%), $\lambda_{\text{max.}}$ 240 mμ (ε 21,750) $\nu_{\text{max.}}$ 1680, 1645, and 1620 cm.$^{-1}$. At the m. p. a yellow sublimate of monomeric quinone condensed on the cooler part of the tube. The infrared spectrum of a sample of the dimer (IV) that had been irradiated with a mercury arc for 12 hr. was unchanged.

The white substance (A) was extracted with light petroleum (b. p. 40—60°) in a Soxhlet apparatus for several days; a pale yellow extract was obtained, which yielded more dimer (IV). The white, insoluble solid, purified by vacuum-sublimation, had an infrared spectrum identical with that of the box-dimer (VIII) made by irradiation with a mercury arc, the yield in the latter process being much smaller.

The yields of dimers (IV) and (VIII) obtained by sunlight irradiation varied according to the length of exposure and the amount of sunlight. Optimum yields were: *trans*-dimer (IV) *ca.* 40%; box-dimer (VIII) *ca.* 2%; recovered quinone *ca.* 40%.

The white solid, insoluble in ether, collected from many irradiations of the quinone with a

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[13] Smith, *Org. Synth.*, **10**, 40.

[14] Teuber and Rau, *Chem. Ber.*, 1953, **86**, 1036.

mercury arc, was extracted (Soxhlet) with ethyl acetate for 6 days. Colourless needles of the box-dimer (VIII), 1,4,7,10-*tetramethylpentacyclo*[6,4,0,0^{2,7},0^{4,11},0^{5,10}]*dodeca*-3,6,9,12-*tetraone*, separated from the concentrated solution. They decomposed at about 250°, when the yellow monomer sublimed up the tube leaving a dark residue. At 240°/20 mm. the compound sublimed to a white powder (Found: C, 70·8; H, 6·0%); it had $\nu_{max.}$ 1700 cm.$^{-1}$ (with shoulder at 1715 cm.$^{-1}$).

This, and the other two box-dimers described below, rapidly absorbed moisture from the air, even in the crystalline state. Samples then absorbed strongly in the regions of 3300 and 1040 cm.$^{-1}$ and the frequency of the C=O vibration fell. Correct analyses were obtained only when freshly sublimed samples were sealed and preserved packed in silica gel. A 12 month-old sample of box-dimer (VIII) had an infrared spectrum with $\nu_{max.}$ 1690, 1030, and 3300 cm.$^{-1}$. A sample recrystallised from ethyl acetate and dried in air gave analyses for a *dihydrate* (Found: C, 62·7; H, 6·5. $C_{16}H_{16}O_4,2H_2O$ requires C, 62·3; H, 6·5%).

Pyrolysis.—The dimer (VIII) was slowly vaporised at 235° in a stream of nitrogen (4 cm. Hg pressure) that passed through a furnace at 500° and then through a cold trap. The unfractionated product had an infrared spectrum identical with that of 2,5-dimethylbenzoquinone. A mixture of 5% of 2,3-dimethylbenzoquinone in the 2,5-dimethylquinone clearly showed a peak at 830 cm.$^{-1}$ due to the 2,3-isomer.

Irradiation of 2,3-*Dimethylbenzoquinone*.—The crystalline quinone was exposed to sunlight and then extracted with boiling ether. The cream-coloured solid (B) was removed and the filtrate evaporated. On chromatography of the residue on silica gel, unchanged quinone passed through in benzene. Benzene containing 10% of ethyl acetate eluted the *cis*-dimer (VI), 1α,2α,7α,8α-4,5,10,11-*tetramethyltricyclo*[6,4,0,0^{2,7}]*dodeca*4,10-*diene*-3,6,9,12-*tetraone*, which crystallised from ether in pale yellow cubes, m. p. 163—164° (without decomposition or sublimation) (Found: C, 70·5; H, 5·85%), $\lambda_{max.}$ 248 mμ (ε 17,570), $\nu_{max.}$ 1677 and 1607 cm.$^{-1}$ (cf. Table).

The extract from several days' Soxhlet-extraction of the solid (B) yielded more of the dimer (VI). The insoluble white residue of the box-dimer (IX), 1,2,7,8-*tetramethylpentacyclo*-[6,4,0,0^{2,7},0^{4,11}0^{5,10}]*dodeca*-3,6,9,12-*tetraone*, was purified by sublimation at 240°/20 mm. (Found: C, 70·25; H, 5·8%). It began to decompose at *ca.* 270° with formation of a trace of yellow sublimate. The sublimed dimer had $\nu_{max.}$ 1710 cm.$^{-1}$; the colourless needles that crystallised from ethyl acetate had $\nu_{max.}$ 1700, 1035, and 3270 cm.$^{-1}$.

Further irradiation of the *cis*-dimer (VI) with a mercury lamp gave a quantitative yield of the box-dimer (IX).

In a typical experiment, 2,3-dimethylbenzoquinone (5·5 g.) was exposed to winter sunshine for about 2 hr., and the yields obtained were: recovered quinone (2·3 g.) 42%; *cis*-dimer (VI) (1·4 g.) 26%; box-dimer (IX) (0·11 g.) 2%. Longer illumination increased the yield of box-dimer (IX) at the expense of (VI). Light from a mercury arc gave a much lower yield of (VI) (about 10%), and a greater yield of (IX) (about 5%) for a 24 hr. irradiation.

Pyrolysis.—The box-dimer (IX) at 240° was vaporised in a slow stream of nitrogen at 8 cm. passing through a tube heated at 510°. The total product collected in the cold trap had a spectrum superimposable on that of 2,3-dimethylbenzoquinone. A synthetic mixture of 5% of 2,5-dimethylbenzoquinone in the 2,3-isomer had a spectrum that clearly showed peaks due to the former at 1350, 1250, 1005, and 920 cm.$^{-1}$.

Irradiation of 2,6-*Dimethylbenzoquinone*.—After 1—2 hours' exposure to sunlight the quinone had faded to a pale yellow colour and the product was quickly extracted with cold ether. The pale yellow solid that was filtered off was immediately crystallised from ether. The pale yellow crystals of 1α,2β,7β,8α-1,2,4,11-*tetramethyltricyclo*[6,4,0,0^{2,7}]*dodeca*-4,10-*diene*-3,6,9,12-*tetraone* (II) (70% yield) had m. p. 84°, $\nu_{max.}$ 1677 and 1640 cm.$^{-1}$. Above the m. p. the dimer dissociated to the monomer, which sublimed up the tube in yellow crystals, m. p. 71—72°. A mixture of monomer and dimer melted at 69—71°, the slightness of the depression being presumably due to rapid dissociation to the monomer in the melt. In boiling benzene the dimer soon dissociated. The ultraviolet spectrum of a dilute solution of the dimer in ethanol measured at intervals showed slow dissociation to the monomer at room temperature; time, $\lambda_{max.}$, and "ε" (calculated as dimer) were: 25 min., 246 mμ, 22,800; 50 min., 247 mμ, 22,800; 4 hr. 25 min., 252 mμ, 25,900; 24 hr., 254 mμ, 32,100; 84 hr., 255 mμ, 34,500. The quinone has $\lambda_{max.}$ 255 mμ, ε 18,300.

When the illuminated quinone was extracted with boiling ether a small amount (about

0·5% yield) of the insoluble box-dimer (VII), 1,5,7,11-*tetramethylpentacyclo*[6,4,0,$0^{2,7}$,$0^{4,11}$,$0^{5,10}$]-*dodeca*-3,6,9,12-*tetraone*, remained. It was purified by sublimation at 225—235°/20 mm., then having $\nu_{max.}$ 1700, 1715(sh) cm.$^{-1}$ (Found: C, 70·7; H, 5·9%). At atmospheric pressure the dimer (VII) sublimed unchanged at 240—300°. At 300° it began to decompose, forming only a trace of volatile yellow product.

Pyrolysis.—The vapour of the dimer (VII), preheated to 200°, was passed in a stream of nitrogen through a furnace at 450°. The yellow needles of quinone in the cold trap were dissolved in ether. Analysis by gas chromatography on silicone at 150° showed only one sharp peak, corresponding to 2,6-dimethylbenzoquinone. A mixture of 2,6-dimethyl- 70%, tetramethyl- 15%, and unsubstituted benzoquinone 15% gave three well-separated peaks in the correct ratio.

Chromatography of the ether extract from sunlight-irradiated quinone on silica gel in ether yielded the unstable dimer (II) and regenerated quinone, followed by the *cis*-dimer (III), 1α,2α,7α,8α-1,5,7,11-*tetramethyltricyclo*[6,4,0,$0^{2,7}$]*dodeca*-4,10-*diene*-3,6,9,12-*tetraone* (5% yield). It separated from ether in pale yellow cubes, m. p. 166—168°, $\lambda_{max.}$ 238 mμ (ε 15,000), $\nu_{max.}$ 1685, 1662, and 1630 cm.$^{-1}$ (Found: C, 71·0; H, 6·1%). It did not decompose or sublime at 200° at atmospheric pressure.

Irradiation of 2,6-dimethylbenzoquinone with a mercury arc for 36 hr. gave small yields of the dimers (III) and (VII). Chromatography on a silica gel column of the residue obtained on evaporation of the ether extract gave with benzene as eluent a 76% yield of recovered quinone. With 10% of ethyl acetate in benzene, the *cis*-dimer (III) was obtained (0·5%). Irradiation of the *cis*-dimer (III) with the arc for 1 hr. caused considerable bleaching, and continued irradiation led to quantitative conversion into the colourless box-dimer (VII) (identical infrared spectra). Similar irradiation of crystals of the unstable dimer (II) turned it green after about ½ hr., although its infrared spectrum was unchanged. On further irradiation the colour gradually changed to yellowish-brown: the same peaks persisted in the spectrum but became more and more diffuse.

Enolisation of the cis-*Dimer* (VI).—The *cis*-dimer (VI) (0·76 g.) was dissolved in ethanol (60 ml.), and a few drops of 2·0N-aqueous sodium hydroxide were added with shaking. The colour of the solution immediately changed from pale yellow to dark brown. After 2 hr., the solution was acidified with a few drops of dilute sulphuric acid, becoming deep yellow. It was then diluted with water and extracted with ether, the ether extract being washed in turn with sodium hydrogen carbonate solution and water. It was then dried (Na_2SO_4) and evaporated to a brown gum, which was chromatographed in benzene on silica gel. Elution with benzene containing 5% of ethyl acetate gave 3,6-*dihydroxy*-1α,8α-4,5,10,11-*tetramethyltricyclo*[6,4,0,$0^{2,7}$]*dodeca*-2,4,6,9-*tetraene*-9,12-*dione* (V) that crystallised as orange-red needles (0·19 g.), m. p. 225—226°, from methanol. The red needles were converted into a yellow, powdery form on drying *in vacuo* (Found: C, 70·4; H, 5·9%); they had λ 219 (ε 15,800sh), $\lambda_{max.}$ 256 (ε 12,100), λ 284 (ε 2500sh), $\lambda_{max.}$ 403 mμ (ε 616), $\nu_{max.}$ 1662, 1618, 1088, and 3330 cm.$^{-1}$.

Compound (V) (50 mg.) was dissolved in a 4 : 1 mixture (5·0 ml.) of pyridine–acetic anhydride. After a few minutes the orange colour began to fade, and soon the solution was almost colourless. About 12 hr. later the mixture was poured into water and extracted with ether, the ether extract being washed in turn with dilute sulphuric acid, aqueous sodium hydrogen carbonate, and water. It was then dried (Na_2SO_4) and evaporated to a white solid, which was chromatographed in benzene on silica. Elution with 5% of ethyl acetate in benzene gave the *diacetate* as very pale yellow crystals [from light petroleum (b. p. 40—60°)] (32 mg.), m. p. 165—166° (Found: C, 67·7; H, 5·5. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%), $\lambda_{max.}$ 255 (ε 12,400), 368 mμ (ε 207), $\nu_{max.}$ 1762, 1675, and 1615 cm.$^{-1}$.

Tetramethyl 2,7-Dioxotricyclo[6,2,0,$0^{3,6}$]decane-4,5,9,10-tetracarboxylate [10] (XII) [m. p. 239° (decomp.); $\nu_{max.}$ 1757, 1739, and 1717 cm.$^{-1}$; no intense ultraviolet absorption above 210 mμ] was vaporised in a stream of nitrogen and passed through a silica tube heated at 650°. A pale yellow solid was deposited on the cooler parts of the exit tube. Colourless crystals separated by fractional sublimation down the tube had m. p. 101—102°, unchanged when mixed with dimethyl fumarate. Their infrared spectra were also identical. The condensate from the bend in the exit tube and from the cold (liquid oxygen) trap had a pungent smell like that of benzoquinone, although its presence could not be confirmed by infrared spectra. In a control experiment a 1 : 1 mixture of dimethyl fumarate and benzoquinone passed through the furnace almost unchanged.

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