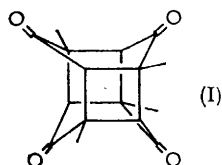


### 457. *Liquid-phase Photolysis. Part VII.<sup>1</sup> Cage-dimerisation of p-Benzoquinone.*

By D. BRYCE-SMITH and A. GILBERT.

Ultraviolet irradiation of *p*-benzoquinone in molten maleic anhydride gives a dimer of the quinone, m. p. 248° (decomp.), shown to be pentacyclo-[6,4,0,0<sup>2,7</sup>,0<sup>4,11</sup>,0<sup>5,10</sup>]dodeca-3,6,9,12-tetraone (III). *p*-Benzoquinone does not undergo photoaddition to benzene, naphthalene, anthracene, or phenanthrene under a variety of conditions. Irradiation of a mixture of *p*-benzoquinone and acenaphthylene gives a copolymer of approximate formula (*p*-benzoquinone)<sub>14</sub>(acenaphthylene)<sub>15</sub>.

COOKSON AND HUDEC obtained a colourless saturated photo-dimer of 2,5-dimethyl-1,4-benzoquinone, and formulated it as (I).<sup>2</sup> Cookson, Cox, and Hudec subsequently



(I)

described in some detail analogous dimers of 2,3- and 2,6-dimethyl-1,4-benzoquinone.<sup>3</sup> Flaig, Salfeld, and Llanos also reported the formation of a colourless photodimer from 2,3-dimethyl-1,4-benzoquinone,<sup>4</sup> and proposed a structure which differed in the positions of methyl groups from that given by Cookson *et al.*<sup>3</sup> In view of the apparent conflict of experimental evidence, there is some doubt whether the dimers obtained by these two groups of workers were identical.

Irradiation of *p*-benzoquinone itself under various conditions has been reported to give a polymer containing hydroxyl groups, but no dimer.<sup>3</sup>

In view of the ease with which maleic anhydride undergoes photoaddition to benzene,<sup>5</sup> we have investigated the possibility that *p*-benzoquinone would add in an analogous

<sup>1</sup> Part VI, Bryce-Smith and Lodge, *J.*, 1963, 695.

<sup>2</sup> Cookson and Hudec, *Proc. Chem. Soc.*, 1959, 11.

<sup>3</sup> Cookson, Cox, and Hudec, *J.*, 1961, 4499.

<sup>4</sup> Flaig, Salfeld, and Llanos, *Angew. Chem.*, 1960, 72, 110.

<sup>5</sup> Angus and Bryce-Smith, *Proc. Chem. Soc.*, 1959, 326; *J.*, 1960, 4791; Bryce-Smith, Gilbert, and Vickery, *Chem. and Ind.*, 1962, 2060; Grovenstein, Rao, and Taylor, *J. Amer. Chem. Soc.*, 1961, 83, 1075; Schenck and Steinmetz, *Tetrahedron Letters*, 1960, No. 21, 1.

manner. In fact, no photoadducts could be obtained from *p*-benzoquinone and benzene, naphthalene, or phenanthrene, with or without the use of benzophenone as sensitiser. Even anthracene and *p*-benzoquinone gave only tarry matter when irradiated at 35°, and no trace of the well-known thermal adduct was found. In contrast, the rate of formation of the thermal adduct of maleic anhydride and anthracene is increased by ultraviolet irradiation.<sup>6</sup> Irradiation of acenaphthylene and *p*-benzoquinone gave an orange copolymer which, from analysis and molecular-weight determination, could be approximately formulated as (*p*-benzoquinone)<sub>14</sub>(acenaphthylene)<sub>15</sub>. Here, maleic anhydride resembles *p*-benzoquinone in that it also gives a copolymer with acenaphthylene.<sup>7</sup>

From most of the above irradiation experiments, varying small amounts of a very pale yellow solid, m. p. 248° (decomp.), were obtained. This substance was most readily obtained by irradiation of a solution of *p*-benzoquinone in molten maleic anhydride or molten benzophenone at 60–65°; even so, the yields were small. The compound was shown to be a dimer of *p*-benzoquinone (see Experimental section). It was virtually insoluble in all common solvents, including dimethylformamide, but dissolved to the extent of ca. 5% in dimethyl sulphoxide at 20°, from which solvent it was recrystallised. It sublimed at ca. 200°/0.1 mm., the very pale yellow colour persisting in the sublimate. At 250° under nitrogen, it reformed *p*-benzoquinone.

The ultraviolet spectrum of the dimer in ethanol had  $\lambda_{\max}$  290 m $\mu$  ( $\epsilon$  64), which is consistent with a saturated unconjugated tetraketone [cf. cyclohexanone in ethanol,  $\lambda_{\max}$  290 m $\mu$  ( $\epsilon$  15.8)]. No absorption corresponding to the enedione chromophore was detected. The faint yellow colour of the dimer persisted in solution, and arose from unusually long tailing of the 290 m $\mu$  peak, just into the visible. These data exclude any formulation of the compound as an "open" dimer (II), although structures of this type are formed on irradiation of dimethyl-1,4-benzoquinones<sup>2-4</sup> and naphtho-1,4-quinone.<sup>8</sup> Dimerisation by addition of C=O to C=C is likewise excluded, although *p*-quinones readily add in this way to isolated ethylenic bonds in cyclohexene and many other olefins, even in sunlight.<sup>9</sup> The proton magnetic resonance spectrum of the dimer in dimethyl sulphoxide at 25° showed a single peak at  $\tau$  7.90. This value is reasonably attributable to the  $\alpha$ -tertiary hydrogen in a cyclobutyl ketone derivative, as may be seen from the  $\tau$ -values listed in the Table.

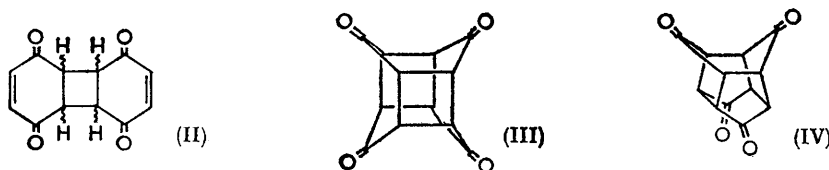
$\tau$ -Values for tertiary hydrogen in di-*s*-alkyl ketones.

Dicyclopropyl ketone .....	8.03	Dicyclohexyl ketone .....	7.13
Dicyclobutyl .....	ca. 7.90 *	Di- <i>isobutyl</i> .....	7.84
Dicyclopentyl .....	7.70	Di- <i>isopropyl</i> .....	7.33

\* Peak largely obscured.

The evidence for a single type of hydrogen taken in conjunction with the ultraviolet and mass-spectral data (see below) excludes all but structures (III) and (IV).

Structure (III) possesses a centre of symmetry and a four-fold axis of symmetry, while



(IV) is not centrosymmetric, but has a four-fold alternating axis of symmetry. A preliminary X-ray crystallographic analysis on a single crystal of the dimer has been carried out.<sup>10</sup> This has excluded the virtually strainless structure (IV) and confirmed

<sup>6</sup> Simons, *Trans. Faraday Soc.*, 1960, **56**, 391; Bryce-Smith and Vickery, unpublished work.

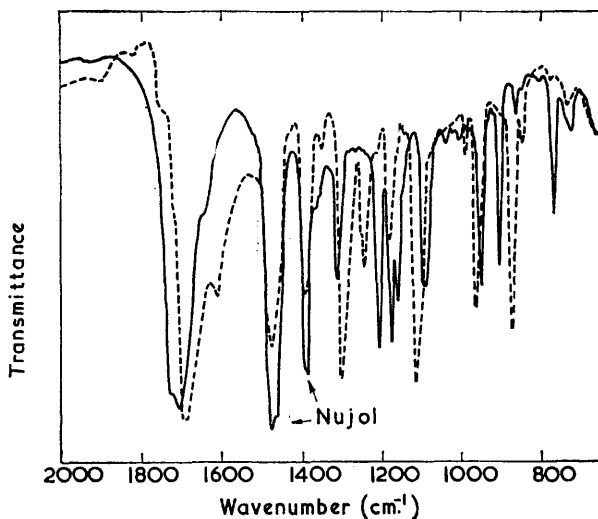
<sup>7</sup> Bryce-Smith, Gilbert, and Vickery, *Chem. and Ind.*, 1962, 2060.

<sup>8</sup> Schonberg, Mustafa, Barakat, Latif, Moubasher, and Said, *J.*, 1948, 2126.

<sup>9</sup> Bryce-Smith and Gilbert, *Proc. Chem. Soc.*, 1964, 87.

<sup>10</sup> Rogers and Gabe (Imperial College, London), personal communication.

structure (III). The results of this analysis are as follows:<sup>10</sup> the crystals are monoclinic tablets with (100) prominent. The unit cell has dimensions  $a = 6.2$ ,  $b = 12.4$ ,  $c = 6.5$  Å,  $\beta = 120^\circ$ , and contains either 4 molecules of benzoquinone or 2 dimeric molecules ( $D_m = 1.6$  g. cm.<sup>-3</sup>;  $D_c = 1.66$  g. cm.<sup>-3</sup>). Systematic absences indicate uniquely the space group  $P2_1/c$ , whose normal complement of equivalent positions is four. Accepting the evidence for dimers, only two can be fitted in this cell if the dimer is centrosymmetric and lies about a centre of symmetry in the cell. Of the likely dimeric forms, only two are centrosymmetric, and one of these, the *trans*-form of structure (II), is promptly ruled out by considerations of packing. The other, (III), is, as the unusually high density suggests, a tight fit in the cell. The possible orientations of the molecule are severely restricted, and it also seems likely that each cyclobutane ring is deformed into a rhombus in order to provide adequate intermolecular C-O clearances. A detailed study of the structure is being attempted.<sup>10</sup>



Infrared spectra: full line, dimer of 2,5-dimethyl-1,4-benzoquinone; dashed line, dimer of *p*-benzoquinone.

The infrared spectrum of the dimer (III) is compared, in the Figure, with that of a dimer of 2,5-dimethyl-1,4-benzoquinone (Nujol mulls), prepared by the procedure of Cookson, Cox, and Hudec, to which structure (I) was attributed.<sup>3\*</sup> We are puzzled by certain differences between these spectra, which, from the proposed structural similarities, seem to be rather greater than would normally be expected, and which, taken in conjunction with the other differences reported below, raise some doubts as to whether the ring system of the dimer of 2,5-dimethyl-1,4-benzoquinone can be unambiguously assumed to be identical with that which we now find for the dimer (III) of *p*-benzoquinone itself.† We have been unable to determine the molecular weight of the dimer of 2,5-dimethyl-1,4-benzoquinone by cryoscopic means, because of its very low solubility in suitable solvents. The

\* A specimen of the dimer of 2,5-dimethyl-1,4-benzoquinone was kindly provided by Professor R. C. Cookson, and had an infrared spectrum identical with that shown in the Figure.

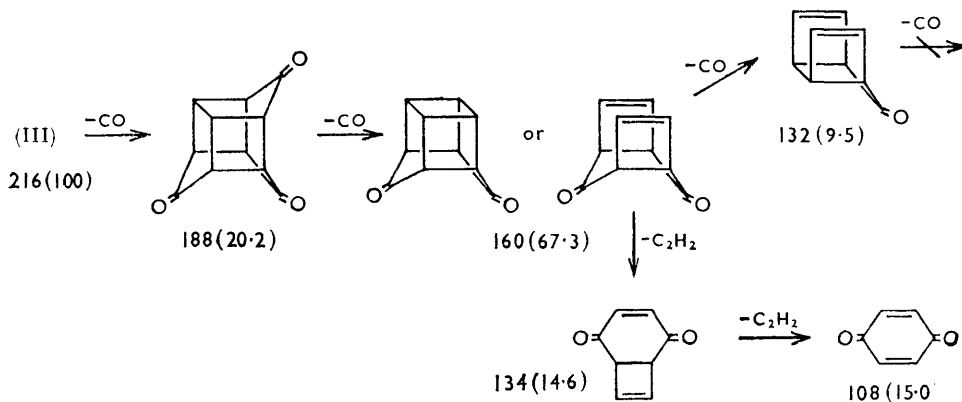
† A referee has suggested that hydrogen atoms and methyl groups attached to a very rigid ring system might show greater differences in their vibrational coupling with it than with less rigid systems. We agree that such differences might well explain the present infrared spectra, but doubt whether they can be generally expected with bridged cyclic systems; for example, the infrared spectra of the moderately rigid adducts of benzene, toluene, and *o*- and *p*-xylene with maleic anhydride are almost indistinguishable in the "fingerprint" region.<sup>11</sup> In our opinion, the spectroscopic and other differences between the saturated dimers of *p*-benzoquinone and 2,5-dimethyl-1,4-benzoquinone now reported do not exclude the possibility of a common ring system; rather do they fail to provide clear confirmation of the structural similarities which might have been expected *a priori* for these compounds.

<sup>11</sup> Bryce-Smith and Gilbert, *J.*, in the press.

heaviest particles detected mass spectrometrically had  $m/e$  272, which corresponds to a dimer. However, the breakdown pattern differed greatly from that of the dimer of *p*-benzoquinone (given below), although the samples were introduced into the mass spectrometer under standardised conditions, and the thermal stabilities of the two compounds were closely similar. All peaks corresponding to particles heavier than monomer ( $m/e$  136) were very small, so we cannot at this stage say with confidence which, if any, of them was the parent.

The abnormally low carbonyl stretching frequency ( $1694\text{ cm}^{-1}$ ) for the solid dimer (III) is noteworthy. Cookson *et al.*<sup>3</sup> reported values of  $1700\text{--}1715\text{ cm}^{-1}$  for three saturated dimers of dimethyl-1,4-benzoquinones. The present low value may mean that the C-C-C angle in the groups C-CO-C is appreciably greater than  $120^\circ$ ;<sup>12</sup> however, if this is so, it is not clear why the corresponding angles for the tetramethyl derivatives should be more normal. Alternatively, the low frequency may result from intermolecular C-H $\cdots$ O hydrogen bonding. Hydrogen attached to saturated carbon does not normally form hydrogen bonds unless the carbon is also linked to strongly electronegative atoms or groups (as in, for example, chloroform<sup>13</sup>). However, the unusually high density ( $1.6\text{ g. cm}^{-3}$ ) of the *p*-benzoquinone dimer indicates that the crystalline structure must involve short contact distances. It has been estimated<sup>10</sup> that adjacent molecules have some C-O separations not greater than  $2.9\text{ \AA}$  and possibly as small as  $2.25\text{ \AA}$ . This seems to imply the possibility of hydrogen bonding. The hydrogen atoms in structure (III), and those attached to strained systems in general, can be expected to be more acidic than those attached to unstrained saturated systems, and therefore more prone to form hydrogen bonds. The conclusion that the low carbonyl stretching frequency arises, at least in part, from hydrogen bonding is supported by the higher (more normal) frequencies found for the tetramethyl derivatives, and by the low frequencies ( $1690\text{--}1700\text{ cm}^{-1}$ ) reported for their hydrates [assuming that the structural assignment, *e.g.*, (I), is correct]. The present dimer, (III), showed no tendency to form a hydrate.

Extrusion of four molecules of carbon monoxide from the dimer (III) could, in principle, give the long-sought "cubane" (pentacyclo[4,2,0,0<sup>2,5</sup>,0<sup>3,7</sup>,0<sup>4,6</sup>]octane). This might have



Unbracketed figures under formulæ represent ( $m/e$ )

been accomplished by means of ultraviolet irradiation; but the dimer (III) proved to be unaffected. In the mass spectrum, no significant peak of  $m/e$  104, corresponding to ["cubane"]<sup>+</sup>, was observed, although there was a significant peak attributable to the loss of three molecules of carbon monoxide. The breakdown pattern given below agrees

<sup>12</sup> Halford, *J. Chem. Phys.*, 1956, **24**, 830.

<sup>13</sup> Bellamy and Williams, *Trans. Faraday Soc.*, 1959, **55**, 14.

well with structure (III). Relative intensities are given in parentheses, and charges are neglected. A peak at  $m/e$  110, relative intensity 27.3, can probably be attributed to quinol. There were no other significant peaks at  $m/e$  values greater than 100, and no metastable peaks were observed.

#### EXPERIMENTAL

*Irradiation of a Solution of p-Benzoquinone in Molten Maleic Anhydride.*—A melt of *p*-benzoquinone (15 g.) and maleic anhydride (20 g.) was irradiated in air, from 15 cm. above, at 60–65° with a 500-w medium-pressure mercury arc lamp for 1 hr. After solidification, the irradiated mixture was digested with diethyl ether. The pale yellow dimer (III), *pentacyclo*-[6,4,0,0<sup>2,7</sup>,0<sup>4,11</sup>,0<sup>5,10</sup>]-*dodeca*-3,6,9,12-*tetraone* (30 mg.), m. p. 248° (decomp.), was filtered off. It formed pale yellow monoclinic tablets from dimethyl sulphoxide [Found: C, 66.6; H, 3.6%; *M* (mass spectrometer), 216. C<sub>12</sub>H<sub>8</sub>O<sub>4</sub> requires C, 66.65; H, 3.7%; *M*, 216]. Analogous results were obtained when benzophenone was used instead of maleic anhydride.

Ultraviolet irradiation of crystalline or molten *p*-benzoquinone produced the same dimer, (III), but in reduced quantities (*ca.* 20 mg. in 1 hr.). An irradiated solution of *p*-benzoquinone in cyclohexane in a water-cooled apparatus<sup>14</sup> produced large quantities of quinhydrone, which, after digesting with diethyl ether, left the insoluble dimer (III) as a residue. Cyclohexene was formed, but no cyclohexa-1,3-diene or benzene was detected (ultraviolet spectrum).

The dimers from all procedures had identical m. p.s (decomp.) and infrared spectra (see Figure). Details of the ultraviolet, proton magnetic resonance, and mass spectra are recorded in the main text. The mass spectra were obtained on an MS 2 spectrometer working at 70 v. Samples were introduced under standard conditions at 250° and 10<sup>-5</sup> mm. pressure.

*Copolymer of p-Benzoquinone and Acenaphthylene.*—A solution of *p*-benzoquinone (15 g.) and acenaphthylene (12 g.) in AnalaR benzene (180 ml.) was irradiated in a water-cooled cell<sup>14</sup> for 12 hr. under a stream of nitrogen. The *p*-benzoquinone was removed by shaking the irradiated solution with 2*N*-sodium hydroxide and then with water. After drying, the resulting benzene solution was chromatographed on alumina (Spence Type H) to give a yellow and an orange band. The yellow band was eluted with benzene and found to contain acenaphthylene only (mixed m. p.), while the orange band could only be eluted with benzene-acetone (3 : 1). Evaporation of the solvent gave an orange solid which decomposed without melting at 165–170° (Found: C, 83.3; H, 4.8%; *M* (cryoscopic in benzene), 3810 ± 95. Calc. for (*p*-benzoquinone)<sub>14</sub>(acenaphthylene)<sub>15</sub>: C, 83.55; H, 4.65%; *M*, 3792).

We thank the late Dr. G. Roberts and Mr. S. Williams for measuring the proton magnetic resonance and mass spectra, respectively, Esso Research Ltd. for laboratory facilities, and the D.S.I.R. for a maintenance grant (to A. G.).

CHEMISTRY DEPARTMENT, THE UNIVERSITY,  
READING, BERKS.

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<sup>14</sup> Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.