

### 558. Application of Nuclear Magnetic Resonance Spectroscopy to Diels–Alder Adducts of *p*-Benzoquinones.

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*cis*- and *trans*-Isomers of 3-methoxypenta-1,3-diene and 3-methoxy-2-methylpenta-1,3-diene have been prepared and the adducts between the *trans*-isomers and several methoxycarbonylbenzoquinones are reported. It has been possible by nuclear magnetic resonance spectroscopy to assign gross structures to the adducts (with one exception), but not their complete stereochemistry.

THERE are few instances<sup>1</sup> in which the mode of addition of a diene to a *p*-benzoquinone has been determined by a stereochemical investigation of the adduct. It is usually assumed that such reactions involve an *endo*-transition state (I), and our results<sup>2</sup> support this. We now suggest a method of determining the complete stereochemistry of certain such adducts, by nuclear magnetic resonance spectroscopy, though we have failed to realise it.

Diels–Alder addition of a *trans*-1-substituted buta-1,3-diene (*cis*-1-substituted dienes add very slowly<sup>1b</sup>) to a substituted *p*-benzoquinone can give, for one structural isomer, two stereoisomeric primary adducts (*i.e.*, no isomerisation after formation). The factors favouring formation of a particular structural isomer have been discussed.<sup>2</sup> *endo*-Addition yields primarily a *syn-cis*-adduct (for example, II), while *exo*-addition will give an *anti-cis*-adduct (III). The adducts (II and III), having one angular substituent, can epimerise only at position 4a: thus the *syn-cis*-adduct (II) can epimerise to the *anti-trans*-structure, and the *anti-cis*- to the *syn-trans*-adduct. The dihedral angle between the tertiary 4a- and 5-hydrogen atoms depends on the stereochemistry of the adduct, and thus upon the mode of addition of the diene to the quinone. The fused-ring system of each *cis*-adduct can exist in two conformations with the cyclohexene ring (on the left as drawn) in the quasi-chair form, while the *trans*-adducts have only one conformation. These are illustrated (IV—VII) by drawing the molecules with 6,7-, 4a,8a-, and 3,2-bonds in Newman projections.

The 5-H/4a-H dihedral angles ( $\phi$ ) in question are: \*

Isomer .....	(IVa)	(IVb)	(V)	(VIa)	(VIb)	(VII)
$\phi$ .....	60°	60°	180°	60°	180°	60°

Karplus<sup>3</sup> and Conroy<sup>4</sup> have established a relation between the dihedral angle ( $\phi$ ) for vicinal protons of this kind and their nuclear magnetic resonance coupling constant ( $J$ ); if  $\phi = 60^\circ$  and  $180^\circ$ , the coupling constants are *ca.* 2 and *ca.* 11 c./sec., respectively. Thus, *endo*-addition of diene and quinone will give rise to a value of  $J \approx 2$  c./sec. for the primary adduct, and  $J \approx 11$  c./sec. for its epimer, while *exo*-addition will lead to  $J \approx 2$  or  $\approx 11$

\* The strain introduced into the molecule by the four *sp*<sup>2</sup>-carbon atoms of the enedione ring requires that the values of  $\phi$  quoted, which are derived from inspection of models, will only be approximate, but they should be sufficiently accurate for the method to be of use.

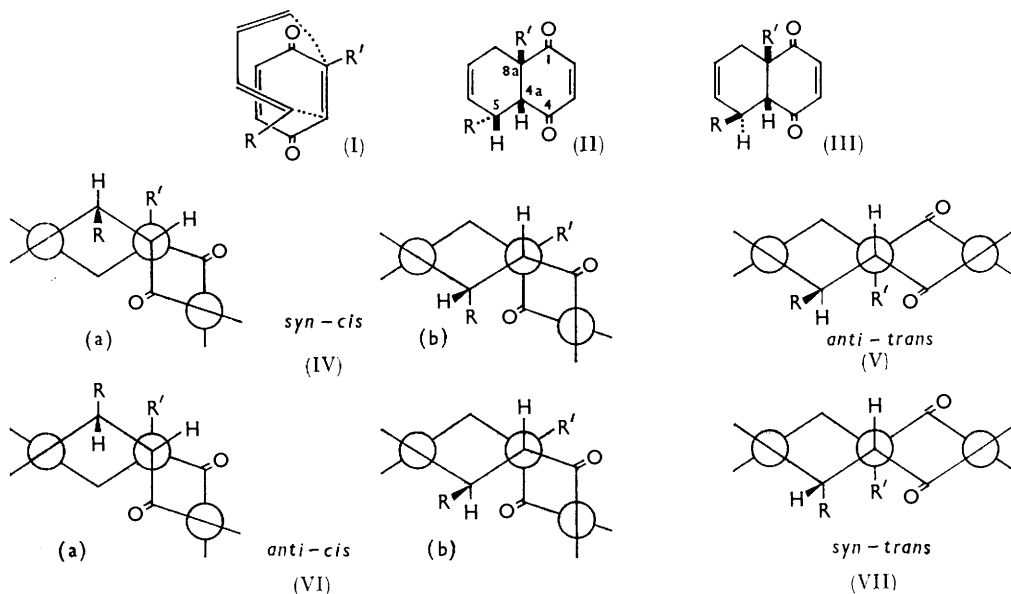
<sup>1</sup> Martin and Hill, *Chem. Rev.*, 1961, **61**, (a) 547, (b) 540.

<sup>2</sup> Ansell, Nash, and Wilson, *J.*, 1963, 3012.

<sup>3</sup> Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

<sup>4</sup> Conroy, *Adv. Org. Chem.*, 1960, **2**, 311.

c./sec. for the primary adduct (if one conformation is much preferred to the other) and  $J \approx 2$  c./sec. for the epimer. An examination of the spectra of pairs of epimers should then provide direct evidence as to the mode of addition. A quasi-boat form of the cyclohexene ring for the *cis*-isomers leads to the same expected changes in  $\phi$  and  $J$ .



The first attempt to use this distinction was made with *trans*-3-methoxypenta-1,3-diene (VIII) and methoxycarbonylbenzoquinone, the adduct (IX; R = CO<sub>2</sub>Me) being expected. So that only one angular hydrogen atom might be present in the adduct, a quinone that would add a diene to its substituted ethene linkage was required; the methoxycarbonyl group is known<sup>2,5</sup> to direct addition in this way. The 5-methyl group was, of course, necessary to provide asymmetry at that point. The 6-methoxy-group served a dual purpose: it would prevent any coupling between the 5-proton and any 6-proton, and it should also direct addition to give the adduct shown (by making C-1 of the diene slightly positive; cf. XVI) and not the adduct with R at position 4a. The results of Beyler and Sarett<sup>6</sup> suggested that this would be the case.

The ethoxy-homologue of (VIII) is known,<sup>7</sup> and an analogous method was used to prepare the diene (VIII) and its *cis*-isomer. Methyl orthoformate, in methanol with a trace of acid, and ethyl vinyl ketone gave 1,3,3-trimethoxypentane, which was pyrolysed to give a mixture of *cis*- and *trans*-3-methoxypenta-1,3-diene. These isomers were readily separated by fractional distillation, and the stereochemical assignments were based on their Diels-Alder reactivity and ultraviolet absorption spectra (see below). With benzoquinone, the *trans*-diene gave an adduct (IX; R = H) which was not very stable at room temperature (cf. ref. 6) but could be kept for several months at 0°. With methoxycarbonyl-1,4-benzoquinone, this *trans*-diene gave an adduct to which is assigned the structure (IX; R = CO<sub>2</sub>Me) by analogy with the work of Beyler and Sarett.<sup>6</sup> The nuclear magnetic resonance spectra of these two adducts were too complex for satisfactory analysis (see p. 3040), owing mainly to the coupling between the 7-H and the 5-H through the allylic system.

<sup>5</sup> Ansell and Culling, *J.*, 1961, 2908.

<sup>6</sup> Beyler and Sarett, *J. Amer. Chem. Soc.*, 1952, **74**, 1397.

<sup>7</sup> Sarett, Lukes, Poos, Robinson, Beyler, Vandergrift, and Arth, *J. Amer. Chem. Soc.*, 1952, **74**, 1393.

To overcome this difficulty, the diene (X) was synthesised (with its *cis*-isomer), and the Diels–Alder reactions between it and benzoquinone and five quinones (XI) were carried out. For *endo*-addition of the diene to the methoxycarbonyl-substituted side of these quinones, groups R and R' would, in the transition states, come close to substituents on the 2- and 3-positions of the diene, and any non-bonded interaction<sup>2</sup> between them might alter the course of the addition.

Methyl orthoformate, in methanolic acid, and 2-methylpent-1-en-3-one gave the corresponding methyl ketal, and not the expected trimethoxyhexane. Pyrolysis of the ketal gave mixtures of *cis*- and *trans*-3-methoxy-2-methylpenta-1,3-diene, which were separated by preparative-scale gas–liquid chromatography. Again, the stereochemical assignments were based in Diels–Alder reactivity and ultraviolet absorption spectra of the dienes. The absorption maxima and extinction coefficients of the two pairs of dienes are:

		$\lambda_{\max}$ . (m $\mu$ ) (and $\epsilon$ )
3-Methoxypenta-1,3-diene .....	<i>cis</i>	208 (9400) and 249 (11,500)
	<i>trans</i>	233 (22,000)
3-Methoxy-2-methylpenta-1,3-diene .....	<i>cis</i>	206 (2750) and 238 (2300)
	<i>trans</i>	228 (17,000)

While the *trans*-dienes can assume planar cisoid or transoid conformations, the *cis*-dienes can assume planar cisoid conformations only with difficulty,<sup>1b</sup> while the transoid conformation for the *cis*-methoxymethylpentadiene also seems to be sterically hindered to some extent, with a consequent low value<sup>8</sup> for the extinction coefficient at 238 m $\mu$ .

The two new methoxy-quinones (XI<sub>d</sub> and e) were prepared by oxidation of the corresponding quinols with silver oxide; although the quinones (XI<sub>a</sub>, b, and c) are unstable<sup>9,10</sup> the two quinones (XI<sub>d</sub> and e) were stable.

With benzoquinone, *trans*-3-methoxy-2-methylpenta-1,3-diene gave a light-sensitive adduct (XII); its nuclear magnetic resonance was not measured and no attempts were made to epimerise it, since it could epimerise at both C-4a and C-8a. Addition of the same *trans*-diene to methoxycarbonylbenzoquinone (XI<sub>a</sub>) gave the adduct (XIII<sub>a</sub>). The methoxycarbonyl group was shown to be at position 4a (rather than 8a) by the nuclear magnetic resonance spectrum (see below) which showed two vinyl protons (on C-2 and C-3) and the 8,8a-system of three protons. Whilst the gross structure of the adduct between an unsymmetrical quinone and an unsymmetrical diene was determined, the original stereochemical investigation was halted for the lack of a 4a-proton. However, the resonance results could be correlated with the presumed stereochemistry (*syn-cis*, as shown) and the study was continued, but with a somewhat modified objective. The *syn*-relation between 5-H and 4a-CO<sub>2</sub>Me resulting from *endo*-addition will be assumed although no direct evidence for it was available.

The *syn-cis*-adduct (XIII<sub>a</sub>), in benzene solution, was chromatographed on alkaline alumina, giving an excellent yield of the epimeric *syn-trans*-adduct (XIV<sub>a</sub>). Again, the stereochemistry is assumed by analogy with other similar epimerisations, but the nuclear magnetic resonance results support the assignment.

2-Methoxycarbonyl-6-methylbenzoquinone (XI<sub>b</sub>) and the same diene gave the *syn-cis*-adduct (XIII<sub>b</sub>) in good yield, and alkaline alumina again effected epimerisation to the *syn-trans*-adduct (XIV<sub>b</sub>) in high yield. The structures were again demonstrated by the nuclear magnetic resonance spectra; the ultraviolet absorption of both adducts ( $\lambda_{\max}$ . ca. 245 m $\mu$ ) provided evidence<sup>11</sup> for the angular nature of the methoxycarbonyl group. In contrast, 2-methoxycarbonyl-5-methylbenzoquinone (XI<sub>c</sub>) and the same diene, under the same conditions, gave only an intractable oil, the ultraviolet absorption of which

<sup>8</sup> Braude and Waight, *Progr. Stereochem.*, 1954, **1**, 138.

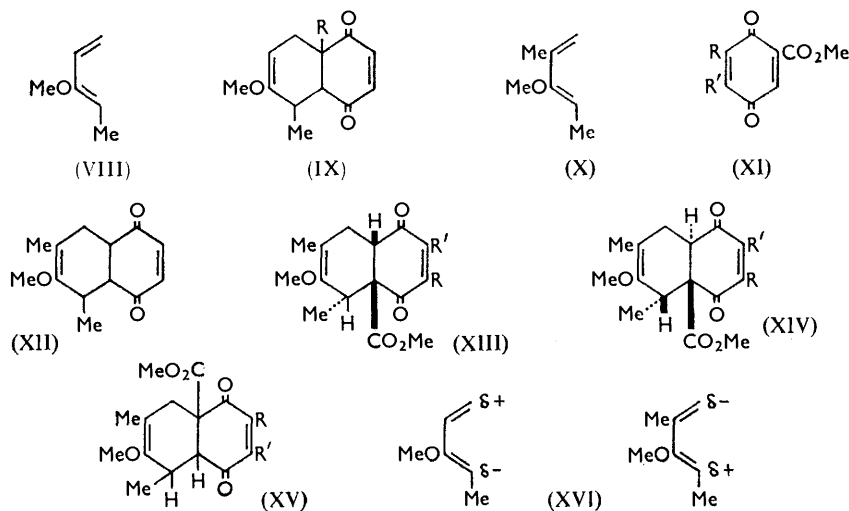
<sup>9</sup> Cason, *Org. Reactions*, 1948, **4**, 354.

<sup>10</sup> Nudenberg, Gaddis, and Butz, *J. Org. Chem.*, 1943, **8**, 500.

<sup>11</sup> Ref. 2, Table 1.

suggested that it contained unchanged quinone and adducts of the gross structure (XIIIc). Chromatography on alumina afforded an oil which was not contaminated by quinone and had the light absorption characteristics and gave analyses for the adduct (XIIIc or XIVc). No solid adduct could be obtained from this reaction, but no nuclear magnetic resonance measurements were made on the oils.

2-Methoxy-5-methoxycarbonylbenzoquinone (XI<sub>d</sub>) and *trans*-3-methoxy-2-methylpenta-1,3-diene gave, in high yield, the *syn-cis*-adduct (XIII<sub>d</sub>) which was epimerised by alkaline alumina to the *syn-trans*-adduct (XIV<sub>d</sub>). Again the ultraviolet absorption of



a: R = R' = H. b: R = Me, R' = H. c: R = H, R' = Me. d: R = H, R' = MeO. e: R = MeO, R' = H.

these adducts ( $\lambda_{\max}$  ca. 273  $m\mu$ ) confirmed<sup>11</sup> the structural assignments based on nuclear magnetic resonance evidence. 2-Methoxy-6-methoxycarbonylbenzoquinone (XI<sub>e</sub>) and this diene gave, at first, an oil, but treatment with alumina gave the *syn-trans*-adduct (XIV<sub>e</sub>) in high overall yield. The very close similarity of the nuclear magnetic resonance spectra of the primary adducts, and of the epimers, is evidence that all the quinones added to the diene through analogous transition states (*i.e.*, *endo*-addition; non-bonded repulsions between diene and quinone substituents having little effect).

If the polarity of the diene controls the relative positions of the methoxy- and methoxycarbonyl groups in the Diels–Alder adducts from the quinones (XI), then the dienes (VIII) and (X) are polarised in opposite directions (XVI) [the diene (VIII) being assumed to be polarised in the same sense as its ethoxy-homologue<sup>6,7</sup>] and the methoxy-groups will tend to polarise in directions opposed by the methyl groups; in the diene (X) the methyl groups are in command, while in (VIII) it is probable that the methoxy-group is determinant.

*Nuclear Magnetic Resonance Results and Discussion.*—Fraser<sup>12</sup> recently determined the configuration of Diels–Alder adducts by using the diamagnetic anisotropy screening of the carbon–carbon double bond in nuclear magnetic resonance. Such an approach is not possible with adducts of quinones because of strong shielding from other groups, notably the carbonyl group.<sup>13</sup> We used the alternative approach of measuring coupling constants, referring to the Karplus relation<sup>3</sup> to deduce the corresponding dihedral angles. Since Anet's work<sup>14</sup> has pointed out the dangers of measuring simple spacings and equating

<sup>12</sup> Fraser, *Canad. J. Chem.*, 1962, **40**, 78.

<sup>13</sup> Crombie and Lown, *Proc. Chem. Soc.*, 1961, 299.

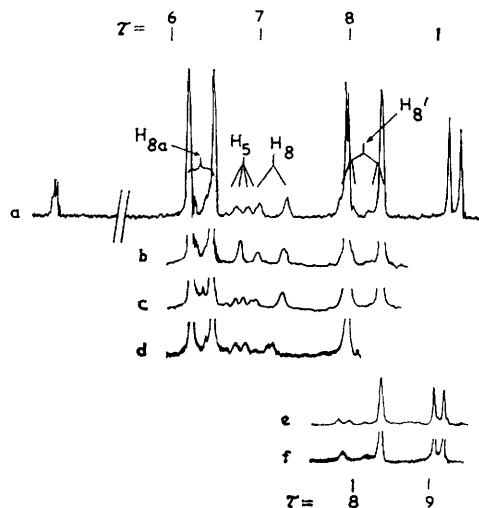
<sup>14</sup> Anet, *Canad. J. Chem.*, 1961, **39**, 2262.

them to coupling constants, it was necessary to use spin-decoupling to obtain true coupling constants; this also has the advantage of leading to unambiguous assignments of chemical shifts.

*General Features of the Spectra.*—The gross features of the spectra (such as those due to methyl and methoxy-groups, and vinyl protons) are readily assigned from considerations of chemical shifts, relative intensities, and general experience. The individual protons associated with the ring junctions were located by spin-decoupling.<sup>15</sup> The chemical shift of the 5-proton, for example, is obtained by measuring the spin-decoupling frequency from the 5-methyl group centre of gravity.

Since interpretation of the spectra of the adducts (IX; R = H or CO<sub>2</sub>Me) is similar to the present discussion, these spectra will not be examined in detail. It suffices to say that systematic line assignment and application of double resonance showed the 5-proton peak to be broadened considerably by allylic coupling to the 7-proton, which prevented measurement of a true coupling constant.

*Stereochemistry of the Adducts (XIII and XIV).*—In the series of adducts (XIII), the gross structures could have been either (XIII) or (XV). Integration of the spectrum of (XIIIb) (Fig. a) showed that the four non-methyl, non-vinyl protons are: one near  $\tau$  8.0, two between  $\tau$  7.4 and 6.6, and one near  $\tau$  6.3. One was identified as a quadruplet near  $\tau$  6.85 as the 5-proton by its coupling to the high-field methyl ( $\delta = +130$  c./sec. at 56.445 Mc./sec.) (Fig. b) and the long-range coupling to the vinylic methyl ( $\delta = +82$  c./sec.) (Fig. c). No other splitting of this signal was apparent. The two lines at  $\tau$  7.36 and 7.04 together make one unit intensity and are split by coupling to a proton 55 c./sec. upfield (Fig. d). Lines of the intensity expected for the X component of an AX system were not visible in this spectrum, but in other primary models of this series, where this region is clear of methyl resonance (XIIIa and d), this resonance is seen to be further split (Fig. e), indicating an AMX or three-spin-coupled system, the third component being shown by decoupling (on XIIa,  $\delta = -90$  c./sec.) (Fig. f) to be the single proton hidden under the methyl resonances near  $\tau$  6.2.



In the epimeric series (XIV) the same three-coupled proton system as in the other series is seen, but with different chemical shifts and coupling constants. Instead of an AMX group, we have an AX<sub>2</sub> group. This spectral type is defined by the ratio of

<sup>15</sup> Turner, J., 1962, 847; Freeman and Whiffen, *Mol. Phys.*, 1961, 4, 321; Evans and Maher, *Proc. Chem. Soc.*, 1961, 208; Evans, *Mol. Phys.*, 1962, 5, 183.

$J_{AX} : \delta_{AX}$ , and a theoretical spectrum for (XIVd) based upon a  $J/8$  value of 0.22 taken from Corio's review<sup>16</sup> shows excellent agreement with the experimental spectrum both in line positions and in intensities. These results confirm the view that we are dealing with structures of the general type (XIII and XIV) above, the three protons at position 8 and 8a giving rise to the AMX system in the primary adducts. Evidently epimerisation at position 8a, leading to the secondary adducts, results in a change in spectral type to the  $AX_2$  system. The latter represents an interesting example in which the 8-protons, although not geometrically equivalent, have accidentally coincident chemical shifts and equal coupling constants to the 8a-proton. The measured coupling constants of the 8- and 8a-protons in primary and secondary adducts are summarised in Table 1, together with the other coupling constants found in this work.

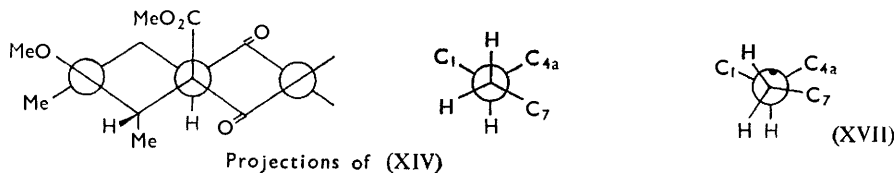
TABLE 1.  
Coupling constants (c./sec.) in primary and secondary adducts.

Adduct	$J_{8,8'}$	$J_{8',8a}$	$J_{8,8a}$	$J_{H,Me}(C-5)$	$J_{2,3}$
XIIIa	19	8	0	7.0	10.2
XIVa	—	9	9	7.5	10.0
XIIIb	17	6	0	7.4	ca. 1
XIVb	—	8.5	8.5	7.0	ca. 1
XIIIc	18	8	0	7.5	—
XIVc	—	8	8	7.0	—
XIVe	—	8	8	7.5	—

The large coupling of 17–19 c./sec. is assignable to the gemi-methylene coupling. We may now attempt to deduce the corresponding dihedral angles. Because of the shape of the Karplus curve, any observed non-zero coupling is ambiguous in that it may correspond to two dihedral angles, one on either side of the curve. Since one coupling constant in the primary adducts is 0 c./sec., we may unambiguously assign the corresponding dihedral angle as *ca.* 90°.

Inspection of Barton models of the *syn-cis*- and the *syn-trans*-forms of the adducts shows that the latter are too rigid to support one dihedral angle of 90° without serious strain, whereas the former, being conformationally more mobile, can accommodate such a dihedral angle in a reasonable conformation. We have rationalised the spectral parameters on this basis, that the primary adducts are *syn-cis*, in agreement with expected Diels–Alder stereochemistry, epimerising to the *syn-trans*-configuration on chromatography.

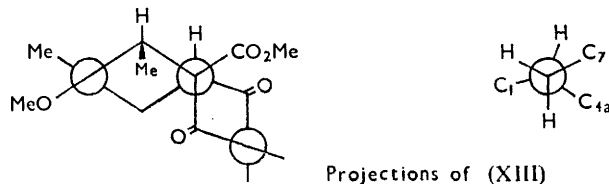
*syn-trans-Series.* The bridgehead proton is assigned in the  $AX_2$  spectrum as the triplet showing equal 8 c./sec. coupling to the methylene protons, since this is the only sharp multiplet, *i.e.*, it shows no long-range coupling to the 7-methyl group. Evidently the preferred conformation is such as to lead to dihedral angles of *ca.* 15° and 135°, as seen in (XVII), a projection of (XIV) along the 8,8a-bond representing couplings of the 8 c./sec. from opposite sides of the Karplus curve.



*syn-cis-Series.* As explained above, in the primary adducts one dihedral angle is fixed at *ca.* 90° and by referring to models the second angle would then be *ca.* 150°, giving an expected coupling of 7.7–8.0 c./sec., in fair agreement with the observed coupling of 8–9 c./sec. throughout the series. In the *syn-cis* configuration, the molecule is fairly

<sup>16</sup> Corio, *Chem. Rev.*, 1960, **60**, 377.

flexible and this implies that the OMe portion of the CO<sub>2</sub>Me group sweeps through the anisotropic shielding cone of the 4-carbonyl group,<sup>13,17</sup> experiencing both positive and negative shielding. In the *syn-trans*-structures on the other hand, which are more rigid,



the methoxyl group will, on average, reside in the positive cone of shielding and suffer a net shift to higher field, as observed (cf. Table 2).

TABLE 2.  
Nuclear magnetic resonance line positions of Diels–Alder adducts (in  $\tau$ -values).

Adduct	2- and/or 3-H	2- or 3-MeO	4a- CO <sub>2</sub> Me	6-MeO	5-H	8a-H	8-H <sub>2</sub>	7-Me	3-Me	5-Me
XIIIa	3.07, 3.28	—	6.22	6.50	6.75	6.22	7.15, 8.0	8.40	—	9.14
XIVa	3.17, 3.39	—	6.34	6.48	6.47	6.78 *	7.62 †	8.38	—	8.92
XIIIb	3.34	—	6.26	6.52	6.85	6.32	7.24, 8.06	8.36	7.97	9.17
XIVb	3.33	—	6.39	6.54	6.49	6.98 *	7.71 †	8.33	7.91	8.94
XIIIc	4.16	6.16	6.25	6.51	6.83	6.33	7.16, 8.13	8.39	—	9.18
XIVc	4.28	6.19	6.38	6.52	6.56	6.98 *	7.68 †	8.42	—	8.99
XIVe	4.07	6.20	6.34	6.50	6.53	6.98 *	7.69 †	8.42	—	8.97

\* Sharp triplet. † Doublet.

### EXPERIMENTAL

Ultraviolet absorption spectra are recorded for ethanol (95%) solutions. Solvents were evaporated below 40° at the water-pump. Nuclear magnetic resonance results for the adducts are not quoted, but are fully discussed in the text. The spectra of compounds (IX) were determined at 56.445 Mc./sec. on a Varian Associates nuclear magnetic resonance spectrometer (model V.4500), for 5–10% solutions in carbon tetrachloride with tetramethylsilane as internal standard, and the line positions are expressed in Tiers's notation.<sup>18</sup> Line positions were measured by the conventional side-band technique, a Muirhead-Wigan decade oscillator D-695-A being used. The spectra of compounds (XIII and XIV) were determined at 60 Mc./sec. on a Varian Associates A-60 analytical spectrometer in the practical conditions described above. The double-resonance experiments were carried out by single side-band modulation, as described by Turner.<sup>15</sup>

**1,3,3-Trimethoxypentane.**—Ethyl vinyl ketone<sup>19</sup> (47.6 g.) and methyl orthoformate (73 g.) were dissolved in dry methanol (102 ml.), and hydrogen chloride (*ca.* 150 mg.) in methanol (2 ml.) was added. The solution was cooled in ice for 15 min., then left at room temperature for 4 days. More methanol (110 ml.) and methanolic acid (2 ml.) were added, and the solution was left for a further 10 days; it was then neutralised with sodium methoxide in methanol, and distilled, to yield, after removal of low-boiling material, 1,3,3-trimethoxypentane (67.7 g., 74%), b. p. 71.5°/17 mm.,  $n_D^{20}$  1.4175 (Found: C, 59.5; H, 11.0. C<sub>8</sub>H<sub>18</sub>O<sub>3</sub> requires C, 59.2; H, 11.2%).

The derived 2,4-dinitrophenylhydrazone (of 1-methoxypentan-3-one) had m. p. 131–131.5° (yellow-orange needles from methanol–chloroform),  $\lambda_{\max}$  372 m $\mu$  ( $\epsilon$  15,900) (Found: C, 48.5; H, 5.4; N, 19.0. C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub> requires C, 48.6; H, 5.4; N, 18.9%). The nuclear magnetic resonance spectrum of the ketal had patterns characteristic of A<sub>2</sub>B<sub>3</sub> and A<sub>2</sub>B<sub>2</sub> groupings, and no doublet that would arise from the 1-protons of the 2,3,3-trimethoxy-isomer.

<sup>17</sup> Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, p. 124.

<sup>18</sup> Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

<sup>19</sup> Woodward, Sondheimer, Taub, Heusler, and McLamor, *J. Amer. Chem. Soc.*, 1952, **74**, 4239.

*cis-* and *trans*-3-Methoxypenta-1,3-diene.<sup>20</sup>—1,3,3-Trimethoxypentane (89 g.) was added during 6 hr. to dried potassium hydrogen sulphate (100 mg.) in a Claisen flask at 170–180°, more sulphate (100 mg.) being added every 30–40 min. The pyrolysate was collected over 20% potassium carbonate solution (30 ml.) containing a little quinol. Light petroleum (b. p. <40°; 200 ml.) was added to the distillate, and the organic layer was separated, washed with 2.5% potassium carbonate solution (2 × 200 ml.), and dried (MgSO<sub>4</sub>). Distillation afforded a fraction (30 g.) of b. p. 100–112° which contained three compounds, in the ratios 4 : 1 : 8 (in order of elution in gas-liquid chromatography; 10% Reoplex on Celite at 30°, argon carrier). The middle component was not identified. A portion of the product was distilled through a spinning-band fractionating column, to give: (a) *trans*-3-methoxypenta-1,3-diene (VIII) (*ca.* 15%), b. p. 97–98°,  $n_D^{20}$  1.4456,  $\lambda_{\max}$  233 m $\mu$  ( $\epsilon$  22,000), 5.50 (C=C overtone), 6.06 (CHR=CH<sub>2</sub>), 6.23 (conj. C=C), 11.03 (CHR=CH<sub>2</sub>), 12.30  $\mu$  (CRR'=CHR') (Found: C, 73.3; H, 10.5. C<sub>6</sub>H<sub>10</sub>O requires C, 73.4; H, 10.3%); [with benzoquinone in benzene, this diene gave an adduct in good yield (cf. next experiment)], and (b) *cis*-3-methoxypenta-1,3-diene (*ca.* 35%), b. p. 110–111°,  $n_D^{20}$  1.4627,  $\lambda_{\max}$  208, 249 m $\mu$  ( $\epsilon$  9400 and 11,500), 5.46 (C=C overtone), 6.07 (CHR=CH<sub>2</sub>), 6.27 (conj. C=C), 10.93 (CHR=CH<sub>2</sub>), 12.61  $\mu$  (CRR'=CHR') (Found: C, 73.05; H, 10.2%). This diene did not react with benzoquinone during 24 hr. at room temperature. A similar pyrolysis gave the dienes in *ca.* 25% yield, in equal proportion.

4a,5,8,8a-Tetrahydro-6-methoxy-5-methyl-1,4-naphthaquinone (IX; R = H).—A solution of benzoquinone (480 mg.) and 3-methoxypenta-1,3-diene (430 mg. containing 42% of *trans*-isomer) in dry benzene (15 ml.) was left at room temperature for 22 hr. The solvent was removed and the yellow residue was kept *in vacuo* overnight, to remove most of the excess of quinone, leaving a pale yellow solid (476 mg., 53%), m. p. 60–72°. Crystallisation from ethanol-light petroleum (b. p. 60–80°) gave the pure *adduct*, m. p. 81–83°,  $\lambda_{\max}$  227 m $\mu$  ( $\epsilon$  10,000) (Found: C, 69.8; H, 7.0. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub> requires C, 69.9; H, 6.8%).

Methyl 1,4,4a,5,8,8a-Hexahydro-6-methoxy-5-methyl-1,4-dioxonaphthalene-8a (or 4a)-carboxylate (?IX; R = CO<sub>2</sub>Me).—A solution of methoxycarbonylbenzoquinone<sup>9</sup> (460 mg.) and 3-methoxypenta-1,3-diene (645 mg. containing 42% of *trans*-isomer) in dry benzene (15 ml.) was left at room temperature for 18 hr. in the dark. Removal of the solvent and crystallisation of the solid residue from ethanol-light petroleum (b. p. 60–80°) gave the pure *adduct* (350 mg., 48%), m. p. 135–137°,  $\lambda_{\max}$  226 m $\mu$  ( $\epsilon$  10,500), 5.77 (ester), 5.90br (enedione C=O), 6.27  $\mu$  (conj. C=C) (Found: C, 63.8; H, 6.1. C<sub>14</sub>H<sub>16</sub>O<sub>5</sub> requires C, 63.6; H, 6.1%). The methoxycarbonyl group is probably at position 8a rather than at 4a (see text).

3,3-Dimethoxy-2-methylpent-1-ene.—2-Methylpent-1-en-3-one<sup>21</sup> (55 g.) and methyl orthoformate (82 g.) were dissolved in dry methanol (120 ml.), and hydrogen chloride (*ca.* 2 mg.) in methanol (3 ml.) was added. The solution was left for 3 days, then more methanol (100 ml.) and methanolic acid (3 ml.) were added, and the solution was left for a further 8 days. It was then made alkaline with sodium methoxide in methanol; fractional distillation afforded 3,3-dimethoxy-2-methylpent-1-ene (46.5 g., 58%), b. p. 140–143°,  $n_D^{20}$  1.4210,  $\lambda_{\max}$  6.06 (CHR=CH<sub>2</sub>), 10.93  $\mu$  (C=CH<sub>2</sub>) (Found: C, 66.8; H, 11.3. C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> requires C, 66.6; H, 11.2%). The derived semicarbazone (of 2-methylpent-1-en-3-one) had m. p. 159–161° (from aqueous methanol), identical (mixed m. p.) with that derived from the authentic ketone (lit.,<sup>21</sup> 161°). The derived 2,4-dinitrophenylhydrazone (of 2-methylpent-1-en-3-one) had m. p. 151–152° (orange-red plates from methanol-chloroform),  $\lambda_{\max}$  378 m $\mu$  ( $\epsilon$  25,000), identical (mixed m. p.) with that derived from the authentic ketone (Found: C, 51.9; H, 4.9; N, 20.0. C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub> requires C, 51.8; H, 5.1; N, 20.1%).

*cis-* and *trans*-3-Methoxy-2-methylpenta-1,3-diene.—3,3-Dimethoxy-2-methylpent-1-ene (38.5 g.) was pyrolysed during 3 hr., by the method described above. Distillation of the product gave a mixture containing three compounds in the ratios 1 : 3 : 1 (gas-liquid chromatography as before). Distillation through the spinning-band column gave only partial separation, but preparative-scale gas-liquid chromatography [column 1.6'' × 13', polypropylene adipate-Embacel (1 : 6, 580 g.) at 64° with nitrogen as carrier gas] gave complete separation and 86% recovery. The last component to be eluted was unchanged ketal. The middle component was *trans*-3-methoxy-2-methylpenta-1,3-diene (X) (*ca.* 35%), b. p. 120–121°,  $n_D^{20}$  1.4539,  $\lambda_{\max}$  228 m $\mu$  ( $\epsilon$  17,000), 5.58, 5.80 (C=C overtones), 6.07 (CRR'=CH<sub>2</sub>), 6.21 (conj. C=C), 11.16

<sup>20</sup> Cf. ref. 7.

<sup>21</sup> Colonge and Cumet, *Bull. Soc. chim. France*, 1947, 838.



(CRR'=CH<sub>2</sub>), 12.29 μ (CRR'=CHR'') (Found: C, 74.7; H, 10.8. C<sub>7</sub>H<sub>12</sub>O requires C, 75.0; H, 10.8%). This diene, with benzoquinone in benzene solution, gave an adduct (see below) in good yield in 24 hr. The first component to be eluted was *cis*-3-methoxy-2-methylpenta-1,3-diene (ca. 11%), b. p. ca. 116—118°,  $n_D^{20}$  1.4357,  $\lambda_{\max}$  238 mμ ( $\epsilon$  2300), 5.50, 5.81 (C=C overtones), 6.06 (CRR'=CH<sub>2</sub>), 6.25 (conj. C=C), 11.02 (CRR'=CH<sub>2</sub>), 12.58 μ (CRR'=CHR''). A satisfactory analysis for this diene was not obtained, but a mixture of *cis*- and *trans*-isomers in a 1:1 ratio (chromatography) gave satisfactory analyses (Found: C, 75.3; H, 10.4%). This diene gave no adduct with benzoquinone; the dienes gave the same 2,4-dinitrophenylhydrazone derivative, identical (m. p. and mixed m. p.) with that obtained from the parent ketal. A similar pyrolysis gave the dienes in the same total yield, but in the ratio 1:4 (*cis*:*trans*).

**2-Methoxy-5-methoxycarbonylbenzoquinone (XIId).**—2,5-Dihydroxy-4-methoxybenzoic acid<sup>22</sup> was heated with methanol containing 3% of concentrated sulphuric acid, giving methyl 2,5-dihydroxy-4-methoxybenzoate (60%), m. p. 145—147° (from methanol) (Found: C, 54.1; H, 5.0. C<sub>9</sub>H<sub>10</sub>O<sub>5</sub> requires C, 54.5; H, 5.1%). The ester (1 g.) was shaken with freshly prepared silver oxide (ca. 4 g.) and anhydrous potassium carbonate (3 g.) in dry benzene (75 ml.) at 40° for 10 min. The mixture was filtered on to anhydrous potassium carbonate, and the residue was washed with more benzene. The filtered solution, on evaporation and crystallisation of the residue from benzene-light petroleum (b. p. 80—100°), afforded the stable orange 2-methoxy-5-methoxycarbonylbenzoquinone (800 mg., 80%), m. p. 116—118°,  $\lambda_{\max}$  5.74 (ester), 5.98, 6.10sh (quinone C=O), 6.15, 6.27 μ (C=C) (Found: C, 55.5; H, 4.45. C<sub>9</sub>H<sub>8</sub>O<sub>5</sub> requires C, 55.1; H, 4.1%).

**2-Methoxy-6-methoxycarbonylbenzoquinone (XIe).**—2,5-Dihydroxy-3-methoxybenzoic acid<sup>23</sup> was esterified, by methanol and sulphuric acid, giving the methyl ester (50%), m. p. 161—163° lit.,<sup>24</sup> 163.5°. The ester was oxidised with silver oxide, as above, giving, after crystallisation from benzene-light petroleum (b. p. 80—100°), the stable orange 2-methoxy-6-methoxycarbonylbenzoquinone (70%), m. p. 126—128°,  $\lambda_{\max}$  5.76 (ester), 5.93, 6.06 (quinone C=O), 6.15, 6.25 μ (C=C) (Found: C, 55.5; H, 3.8%).

**4a,5,8,8a-Tetrahydro-6-methoxy-5,7-dimethyl-1,4-naphthoquinone (XII).**—Benzoquinone (510 mg.) and 3-methoxy-2-methylpenta-1,3-diene (770 mg. containing 88% of *trans*-isomer) in dry benzene (15 ml.) for 24 hr. in the dark, afforded, on removal of the solvent, a solid (607 mg., 58% based on quinone), m. p. 60—73°. Two crystallisations from ethanol-light petroleum (b. p. 60—80°) gave the pure *adduct*, m. p. 72—74°,  $\lambda_{\max}$  228 mμ ( $\epsilon$  11,500) (Found: C, 71.0; H, 7.3. C<sub>13</sub>H<sub>16</sub>O<sub>3</sub> requires C, 70.9; H, 7.3%). This adduct was light-sensitive but could be kept in the dark at 0° for several months.

**Methyl syn-cis-1,4,4a,5,8,8a-Hexahydro-6-methoxy-5,7-dimethyl-1,4-dioxonaphthalene-4a-carboxylate (XIIIa).**—Methoxycarbonyl-1,4-benzoquinone<sup>9</sup> (1 g.) and 3-methoxy-2-methylpenta-1,3-diene (850 mg. containing 88% of *trans*-isomer) were dissolved in dry benzene (15 ml.) and left at room temperature for 22 hr. in the dark. Removal of the solvent and crystallisation of the residue from ethanol-light petroleum (b. p. 80—100°) gave the *syn-cis-adduct* (1.26 g., 75%), m. p. 110—112°,  $\lambda_{\max}$  228 mμ ( $\epsilon$  10,000), 5.72 (ester), 5.93sh, 5.98 (enedione C=O), 6.23 μ (conj. C=C) (Found: C, 64.5; H, 6.65. C<sub>15</sub>H<sub>18</sub>O<sub>5</sub> requires C, 64.7; H, 6.5%).

**Methyl syn-trans-1,4,4a,5,8,8a-Hexahydro-6-methoxy-5,7-dimethyl-1,4-dioxonaphthalene-4a-carboxylate (XIVa).**—The *syn-cis*-adduct (XIIIa) (470 mg.), in benzene, was put on to a column of alkaline alumina (6 × 1 cm.; Peter Spence's type H, 100—200 mesh) and eluted with benzene (45 ml.). Removal of the solvent gave a solid (432 mg., 92%), m. p. 105—110°, which was twice crystallised from ethanol-light petroleum (b. p. 80—100°); it gave the *syn-trans-adduct*, m. p. 111.5—113°,  $\lambda_{\max}$  228 mμ ( $\epsilon$  9500), 5.79 (ester), 5.93 (enedione C=O), 6.24 μ (conj. C=C) (Found: C, 64.8; H, 6.6%). A mixed m. p. with the *syn-cis*-adduct was 85—100°.

**Methyl syn-cis-1,4,4a,5,8,8a-Hexahydro-6-methoxy-3,5,7-trimethyl-1,4-dioxonaphthalene-4a-carboxylate (XIIIb).**—2-Methoxycarbonyl-6-methylbenzoquinone<sup>10</sup> (1 g.) and 3-methoxy-2-methylpenta-1,3-diene (1.3 g. containing 75% of *trans*-isomer) in benzene (15 ml.) (20 hr. in the dark) gave the *syn-cis-adduct* (950 mg., 60%), m. p. 97—99° [from ethanol-light petroleum (b. p. 60—80°)],  $\lambda_{\max}$  246 mμ ( $\epsilon$  10,000), 5.74 (ester), 5.91, 5.99 (enedione C=O), 6.16 μ (conj. C=C) (Found: C, 65.7; H, 6.9. C<sub>16</sub>H<sub>20</sub>O<sub>5</sub> requires C, 65.7; H, 6.9%).

<sup>22</sup> Yates and Stout, *J. Amer. Chem. Soc.*, 1958, **80**, 1691; Rajagopalan, Seshadri, and Varadarajan, *Proc. Indian Acad. Sci.*, 1949, **30**, A, 265.

<sup>23</sup> Schock and Tabern, *J. Org. Chem.*, 1951, **16**, 1772.

<sup>24</sup> Robertson, Whalley, and Yates, *J.*, 1951, 2013.

*Methyl syn-trans-1,4,4a,5,8,8a-Hexahydro-6-methoxy-3,5,7-trimethyl-1,4-dioxonaphthalene-4a-carboxylate* (XIVb).—The *syn-cis*-adduct (XIIIb) (470 mg.) in benzene, on treatment with alkaline alumina as above, gave a solid (414 mg., 88%), m. p. 123—130°, which crystallised from ethanol-light petroleum (b. p. 80—100°) to give the *syn-trans*-adduct, m. p. 131—133°,  $\lambda_{\max}$ . 243 m $\mu$  ( $\epsilon$  8300), 5.80 (ester), 5.90sh, 5.95 (enedione C=O), 6.15  $\mu$  (conj. C=C) (Found: C, 65.8; H, 6.7%).

*Reaction between 2-Methoxycarbonyl-5-methylbenzoquinone and trans-3-Methoxy-2-methylpenta-1,3-diene.*—Oxidation of 2-hydroxy-4-methylbenzoic acid with ammonium persulphate in aqueous alkali (cf. preceding paper) gave 2,5-dihydroxy-4-methylbenzoic acid, m. p. 244—246° (decomp.), which with methanol-sulphuric acid gave the methyl ester, m. p. 123—125°, in a 56% yield. (Previous workers,<sup>10</sup> who prepared the acid by Kolbe-Schmitt carboxylation of toluquinol, recorded m. p. 203—204°. Esterification of this material gave a mixture from which the methyl ester, m. p. 119—122°, was obtained in only 34% yield. Carboxylation of toluquinol thus appears to give a mixture of isomeric acids, from which the above pure acid was not obtained.<sup>10</sup>)

2-Methoxycarbonyl-5-methylbenzoquinone (1.83 g.) and the diene (1.82 g. of *cis*- and *trans*-isomers, 75% of the latter) were dissolved in dry benzene (20 ml.) and left at room temperature overnight. Removal of the solvent gave an orange oil,  $\lambda_{\max}$ . 246 ( $E_{1\text{cm}}^{1\%}$ . 298) (suggesting the expected adduct) and 346 m $\mu$  ( $E_{1\text{cm}}^{1\%}$ . 55) (indicating unchanged quinone). No solid was obtained from the oil, which when chromatographed on alumina in benzene gave a pale yellow oil,  $\lambda_{\max}$ . 246 m $\mu$  ( $\epsilon$  9900 at 246 m $\mu$  for *M* 292), 5.74br, 5.82br (ester?), 5.90, 6.01 (enedione C=O?), 6.16  $\mu$  (conj. C=C) (Found: C, 65.8; H, 6.9. Calc. for C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>: C, 65.7; H, 6.9%). The oil thus contained isomers of the expected adduct, methyl 1,4,4a,5,8,8a-hexahydro-6-methoxy-2,5,7-trimethyl-1,4-dioxonaphthalene-4a-carboxylate.

*Methyl syn-cis-1,4,4a,5,8,8a-Hexahydro-2,6-dimethoxy-5,7-dimethyl-1,4-dioxonaphthalene-4a-carboxylate* (XIIIId).—A solution of 2-methoxy-5-methoxycarbonylbenzoquinone (420 mg.) and 3-methoxy-2-methylpenta-1,3-diene (500 mg. containing 60% of *trans*-isomer) in dry benzene (15 ml.) was left for 42 hr. at room temperature. Removal of the solvent gave a solid, m. p. 134—138°. Crystallisation from ethanol-light petroleum (b. p. 80—100°) gave the *syn-cis*-adduct (550 mg., 83%), m. p. 143—145°,  $\lambda_{\max}$ . 272 m $\mu$  ( $\epsilon$  9800), 5.80 (ester), 5.90, 6.03 (enedione C=O), 6.23  $\mu$  (conj. C=C) (Found: C, 62.2; H, 6.6. C<sub>16</sub>H<sub>20</sub>O<sub>6</sub> requires C, 62.3; H, 6.5%).

*Methyl syn-trans-1,4,4a,5,8,8a-Hexahydro-2,6-dimethoxy-5,7-dimethyl-1,4-dioxonaphthalene-4a-carboxylate* (XIVd).—The *syn-cis*-adduct (XIIIId) (600 mg.), in benzene, on treatment with alumina as above, gave a solid (540 mg., 90%), m. p. 126—135°, which crystallised from ethanol-light petroleum (b. p. 80—100°) to give the *syn-trans*-adduct, m. p. 137—139°,  $\lambda_{\max}$ . 274 m $\mu$  ( $\epsilon$  11,000), 5.80 (ester), 5.83, 6.01 (enedione C=O), 6.23  $\mu$  (conj. C=C) (Found: C, 62.5; H, 6.3%).

*Methyl syn-trans-1,4,4a,5,8,8a-Hexahydro-3,6-dimethoxy-5,7-dimethyl-1,4-dioxonaphthalene-4a-carboxylate* (XIVe).—2-Methoxy-6-methoxycarbonylbenzoquinone (520 mg.) and 3-methoxy-2-methylpenta-1,3-diene (600 mg. containing 60% of *trans*-isomer) in dry benzene (15 ml.) were left at room temperature for 45 hr. Removal of the solvent gave an oil that did not crystallise. Treatment of the oil, in benzene, with alumina as above, and removal of the solvent afforded a solid (580 mg., 70%), m. p. 138—148°. Crystallisation from ethanol-light petroleum (b. p. 80—100°) gave the *syn-trans*-adduct, m. p. 151—153°,  $\lambda_{\max}$ . 278 m $\mu$  ( $\epsilon$  8050), 5.72 (ester), 5.80, 5.93 (enedione C=O), 5.99, 6.23  $\mu$  (C=C) (Found: C, 62.7; H, 6.5%).

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