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## Stereoselective Photochemical Ring-opening of Cyclohexa-2,4-dienones<sup>1</sup>

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The stereoselectivity of the photochemical ring-opening of 6-acetoxy-6-methylcyclohexa-2.4-dienones to derivatives of hepta-3,5-dienoic acid has been shown to be general, and the stereochemistry of the products has been studied by use of n.m.r. long-range coupling and solvent-shift data. Two representative 6-benzoyloxy-analogues behave in a similar manner.

BARTON and QUINKERT<sup>2</sup> showed that u.v. irradiation of representative cyclohexa-2,4-dienones in the presence of nucleophiles (water, alcohols, or amines) usually leads to dienecarboxylic acids, esters, or amides. Arguments were given to support the view that ketens are produced by a valence-isomerisation of the dienone, and trapped (with varying efficiency) by the nucleophiles.<sup>2,3</sup> Ketens have recently been observed directly in low-temperature irradiations of cyclohexa-2,4-dienones, by u.v.,<sup>1,4-6</sup> i.r.,<sup>4-7</sup> and n.m.r.<sup>6</sup> spectroscopy. Their reactions with alcohols 1,7 and amines 6,7 give the products which are found when the dienones are irradiated in the presence of the same nucleophiles.

We have reported that irradiation of 6-acetoxy-2,3,4,5,6-pentamethylcyclohexa-2,4-dienone (VI) gives a single diene-keten stereoisomer, which can cyclise stereoselectively to a bicyclo[3,1,0]hex-3-en-2-one, or be trapped by amines to give an amide.<sup>4</sup> We wished to

- <sup>3</sup> G. Quinkert, Angew. Chem. Internat. Edn., 1965, **4**, 211. <sup>4</sup> M. R. Morris and A. J. Waring, preceding paper.

establish the stereochemistry of the amide (and thus, we argued, of the keten) to allow an analysis of the stereochemistry of the keten-to-bicyclohexenone cyclisation. Irradiations of a series of cyclohexa-2,4-dienones allow a test of the view that the stereoselective ring-opening is reasonably general, and simplify the n.m.r. spectra of the products so that stereochemical assignments can be made.

The 6-acetoxycyclohexa-2,4-dienones (o-quinol acetates) (I)-(X) were prepared by lead tetra-acetate acetoxylation of the corresponding phenols. Wessely and his co-workers found, late in their extensive studies, that chloroform is a better solvent for the reaction than acetic acid.<sup>8</sup> We have confirmed this, and find that in most cases the quinol acetates can be crystallised directly, without the need for prior distillation which can effect thermal rearrangements. Spectroscopic data (Table 1) confirm the o-quinol acetate structures.<sup>†</sup> Ultraviolet

G. Quinkert, Photochem. and Photobiol., 1968, 7, 783.

<sup>6</sup> G. Quinkert, B. Bronstert, P. Michaelis, and U. Krüger, Angew. Chem. Internat. Edn., 1970, **9**, 240. <sup>7</sup> J. Griffiths and H. Hart, J. Amer. Chem. Soc., 1968, **90**,

3297, 5296.

 <sup>8</sup> Reviewed by A. J. Waring in Adv. Alicyclic Chem., 1966, 1, 129; Osterr. Chem.-Ztg., 1967, 68, 232.
 <sup>9</sup> (a) W. Regel and W. v. Philipsborn, Helv. Chim. Acta, 1968, 51, 867; (b) A. A. Bothner-By and E. Moser, J. Amer. Chem. Soc. 1968, 00, 2947 Soc., 1968, 90, 2347

<sup>†</sup> The n.m.r. chemical shifts and coupling constants agree with the ranges given for o-quinol acetates and alkylcyclohexa-2,4dienones by ourselves,<sup>§</sup> Regel and Philipsborn, <sup>94</sup> and Bothner-By and Moser.<sup>90</sup> For summaries of i.r. and u.v. data for such compounds, see ref. 8.

<sup>&</sup>lt;sup>1</sup> Preliminary communication, M. R. Morris and A. J. Waring, Chem. Comm., 1969, 526. <sup>2</sup> D. H. R. Barton and G. Quinkert, J. Chem. Soc., 1960, 1.

				Quinol ac	cetates						
	Мр	Ť ;+		$\tau$ Value of group at position							
Compd.	(°Č)	m.p. (°C)	$\lambda_{max}/nm$	log ε	$\nu_{\rm max.}/{\rm cm^{-1}} b$	$\overline{2}$	3	4	5	6	-OAc
(1)	$79 \cdot 5 - 81$	8284 °	206, 310	$3.79, \ 3.57$	$1740,\ 1677,\\1660$	8·10 d	3.39 d	8·12 d	$4 \cdot 25$ d	8.75	8.03
(11)	$46 - 47 \cdot 5$		207, 307	3.75, 3.58	1743, 1690, 1677, 1659	4.19 d	7.97 d	8·10 d	4.19 d	8.77	8.06
(111)	70 - 72	74 e			$1750, 1680, \\1655$	4·20 d	8.00 d	4·20 ₫	8·20 d	8.70	7.98
(IV)	$62 \cdot 5 - 64$		207, 317	3.82, 3.62	1740, 1680, 1640	4.00 f	$3 \cdot 20^{f}$	8·10 ¢	8·25 g	8.72	7.97
(V)	6061	6466 <sup>k</sup>	217, 314	3.68, 3.73	$1747, \ 1668, \ 1650$	8.17 0	7·98 ø	4·17 d	8·22 d	8.72	7.97
(VI)	8486	87·589·5 h	213, 321	$3.87, \ 3.58$	1735, 1663, 1640	8.12 9	7·98 g	8.12 9	8·25 ¢	8.78	7.98
(VII)	8890		217, 319	4.03, 3.63	1755, 1747, 1670, 1622	8.06 9	7.75 9		8.06	8.70	7.95
(VIII)	9496		209, 316	3.92, 3.58	$1750, 1680, \\1643$	4·20 d	7·94 d	8.14 9	8·26 ¢	8.77	8.00
(IX)	7173	72.5	206, 322	3.71, 3.69	$1754,\ 1681,\\1657$	$4.03^{f}$	3.21 s, j	3.99 j			8.00
$(\mathbf{X})$	98100	101 <sup>i</sup>	207, 318	3.85, 3.82	$1750, 1680, \\1642$	4·11 k	3.13 k.1	3.97 1			7.96

TABLE 1

<sup>a</sup> In 95% EtOH. <sup>b</sup> In CCl<sub>4</sub> solution. <sup>c</sup> F. Wessely and F. Sinwel, Monatsh., 1950, **81**, 1055; F. Wessely and E. Schinzel, *ibid.*, 1953, **84**, 425; E. Zbiral, O. Saiko, and F. Wessely, *ibid.*, 1964, **95**, 512. <sup>d</sup> Methyl and vinyl groups have allylic coupling, *J ca.* 1 Hz. <sup>e</sup> H. Budzikiewicz, G. Schmidt, P. Stockhammer, and F. Wessely, *Monatsh.*, 1959, **90**, 609; J. Leitich and F. Wessely, *ibid.*, 1964, **95**, 116. <sup>f</sup> AB quartet, *J ca.* 10.0 Hz. <sup>e</sup> Methyl signals have homoallylic coupling, *J ca.* 1 Hz. <sup>k</sup> J. Leitich and F. Wessely, *Monatsh.*, 1964, **95**, 129. <sup>i</sup> F. Wessely, J. Kotlan, and W. Metlesics, *Monatsh.*, 1954, **85**, 69. <sup>j</sup> AB quartet, *J ca.* 6 Hz. <sup>k</sup> AB quartet, *J* 9.3 Hz. <sup>i</sup> AB quartet, *J* 7 Hz.

irradiation, through Pyrex, in ether solution containing cyclohexylamine, gave the amides (Ia)—(VIIa) and (IXa) in good yield. In each case g.l.c. analysis of the

0Ac R Me OAc хн OAc R<sup>5</sup> R3. **R**5 CHR<sup>2</sup> 'n4 ċοx -(VIIIa)X = NH-(I)---(VIII) (Ia)cyclohexyl X = OMe(b)  $\mathbf{X} = \mathbf{OEt}$ (c) R³  $\mathbb{R}^4$ R۶  $\mathbb{R}^2$ н Me н Me Me (II) H Me н (III)н Me н Me H н Me Me IVMe Me н Me VI Me Me Me Me Me Me  $\mathbf{Br}$ Me (VII ÌVIII н Me Me Me Ac C OAc 0Ac н Н CH2COX (IXa, b, c) (X) (IX)

crude mixtures showed rapid and clean reaction, with production of a single amide photoproduct, usually a little of the parent phenol (by formal loss of OAc and uptake of a proton), and any unchanged quinol acetate. Monitoring by n.m.r. supported the g.l.c. analyses. Physical data on the amides are given in Tables 2 and 3. Some quinol acetates were irradiated in methanol or ethanol, giving the single ester products (IVb), (VIIIb), (IXb), and (IXc), for which data are given in Tables 2 and 3.

The structures of the amides and esters follow from their i.r. spectra. Enol acetate (1735-1755), secondary amide (3380-3410 and 1670-1675) or saturated ester (ca. 1750 cm<sup>-1</sup>) peaks are similar to those of analogues at 1745-1760, 3360-3385 and 1670-1682, and ca. 1740 cm<sup>-1</sup>. The addition of amines or alcohols to the ketens could occur at the 1,2-, 1,4-, or 1,6-positions; all our n.m.r. evidence supports 1,2-addition. The amides or esters give signals corresponding to the correct number of vinyl protons for the hepta-3,5-dienoic acid structures shown. Dienones (IV) and (IX) give compounds (IVa and b) and (IXa, b, and c) with 2-methylene groups which couple as expected (J ca. 8 Hz) to the 3vinyl proton. Similarly, all the 2-methyldienones, and only they, give amides containing a 2-CH(Me)-grouping which couples as anticipated to any 3-vinyl proton. The chemical shifts of the 2-methylene or methine protons are consistent with the grouping being adjacent to a carbonyl group.\* These results support work on the structures of esters produced in photolyses of other quinol acetates <sup>11</sup>

<sup>10</sup> U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, 1969, **25**, 2023, and references therein.

<sup>11</sup> J. E. Baldwin and M. C. McDaniel, J. Amer. Chem. Soc., 1968, **90**, 6118.

<sup>\*</sup> The 6-Me, OAc, and 5-Me chemical shifts agree with those of simple enol acetates. Literature ranges for simple enol acetates (XII or XIII; Y = OAc), discussed later, are  $\tau 8.08$ -8.22 for methyl  $\alpha$  to the acetate, 7.84-8.03 for acetate, 8.52-8.55for methyl  $\beta$  and *cis* to acetate, and *ca*. 8.40 for methyl  $\beta$  and *trans* to it. The 5-vinyl proton, if *cis* to acetate should be near  $\tau 4.43$ , and if *trans* near 4.67, according to the additivity relationship of Pascual and his co-workers.<sup>10</sup>

and alkylcyclohexa-2,4-dienones.<sup>12</sup> However, we found no evidence for 1,4- or 1,6-addition to the ketens, although some 1,6-addition of methanol has been found by Collins and Hart.<sup>12</sup> It is of interest that amide (Ia) gives a doublet, showing coupling to the 2-proton with J 10.0 Hz; the other (H-5) gives a quartet (J 0.9 Hz) due to coupling to the 6-methyl; these data confirm the structure (Ia).

### TABLE 2

					Ar	nides a	and es	ters				
	Ил	Pn	Found (%)			Required (%)			2 /			Vield
Compd.	(°C)	(°C; mmHg)	C	H	N	C	H	N	nm a	log ε	$\nu_{\rm max,}/{\rm cm^{-1}} b$	(%) °
(Ia) (IIa) (IIIa) (IVa)	$77 - 78^{ d} \\ 81 - 83 \\ 108 - 110 \\ 58 - 60$		$69.5 \\ 69.5 \\ 69.4 \\ 69.9$	9·2 9·0 9·7 9·4		> 69∙6	9.3	4.8	211 210 213 210	3·77 3·80 3·85 3·74	3385, 1740, 1672 3380, 1740, 1670 3380, 1738, 1670 3390, 1740, 1670	$56 \\ 50; > 77 e \\ 41 \\ 50; 80 e$
(IVb) (Va) (VIa) (VIa)	5051 7374 7375 f	98; 1·0	$64 \cdot 0$ 70 \cdot 1 70 \cdot 8 56 \cdot 1		$4.5 \\ 4.5 \\ 3.65$	63·8 70·3 71·0 55·9	8·0 9·5 9·7 7·2	4∙6 4∙4 3∙6	211 207 208 212	3·70 3·93 3·75 3·91	1755, 1685, 1640 3380, 1735, 1670 3380, 1738, 1670 3380, 1738, 1670 3380, 1750, 1670,	$53 \\ 70 \\ > 61 \\ 52$
(VIIIb)		96; 0·6									1758—1748, 1648 4	70
(IXa)	7880		$69 \cdot 8$	8.8	$5 \cdot 1$	<b>70</b> ·0	8.6	4.8	205, 245	4.00, 4.20	3410, 1750, 1670	35
(IXb)			<b>64</b> ·0	<b>8</b> ∙0		<b>63</b> ·8	<b>8</b> ∙0		205, 244	4.02, 4.06	1745, 1658, 1620	87 h
(IXc)									205, 243	3·91, 4·08	1744, 1660, 1620	95 h

<sup>a</sup> In 95% EtOH; the sharp fall in absorption below 210 nm is believed not to be due to solvent cut-off. <sup>b</sup> In CCl<sub>1</sub> solution unless stated otherwise. <sup>c</sup> Yield of crystallised or distilled product. <sup>d</sup> Lit. m.p. 76-79° (D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1960, 1). <sup>e</sup> Yield from quantitative g.l.c., at *ca.* 90% conversion. <sup>f</sup> Found: Br, 20.3. C<sub>18</sub>H<sub>28</sub>BrNO<sub>3</sub> requires Br, 20.7%. <sup>g</sup> Liquid film. <sup>h</sup> Without distillation.

Table	3
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N.m.r. data for amides and esters

	2-Subst.			3-Subst.			4-Subst.			5-Subst.			<b>6-M</b> e		OAc	
Compd.		τ <i>α</i>	Δ <sup>b</sup>			$\Delta$		τ	Δ	(	τ	Δ	τ	$\overline{\Delta}$	τ	Δ
(Ia) °	H Ma	7.06	-0.25	н	4.69	-0.24	Me	8.21	0.18	н	<b>4</b> · <b>4</b> 6	-0.05	<b>8</b> ·22	0.08	7.87	0.47
(XIVa) ª	Me H M-	8.90 6.89	-0.23 -0.26	н	4.63	-0.25	Me	8.16	0.18	н	<b>4</b> ·30	-0.04	8.08	0.11		
(IIa) e	ме Н	7.21	-0.23 -0.18	Me	8.15	-0.12	Me	8.24	0.14	н	<b>4</b> ·38	-0.15	8.24	0.06	7.87	0.47
(IIIa) f	н	7.27	-0.19	Me	8.11	-0.12	н	$4 \cdot 42$	0.08	Me	8.50	-0.04	8.27	-0.03	7.88	0.42
(IVa) 🤊	н	7.30	-0.24	н	4.45	-0.26	Me	8.20	0.12	Me	8.48	0.00	8.30	-0.04	7.85	0.42
(IVb) A	н	7.04	-0.18	$\mathbf{H}$	4.62	-0.12	Me	8.19	0.15	Me	8.46	-0.03	8.32	-0.08	7.92	0.35
(Va) <sup>i</sup>	H Me	$6.85 \\ 8.92$		Me	8.27		Η	4.49		Me	8.54		8.31		7.90	
(VIa) <sup>j</sup>	H Me	$6.92 \\ 8.92$	$-0.32 \\ -0.23$	Me	$\frac{8 \cdot 28}{8 \cdot 30}$	-0.54	Me	$8 \cdot 28 - 8 \cdot 30$	0.07	Ме	8.47	0.02	8·28— 8·30	-0.02	7.82	0.50
(VIIa) *	H Me	6·85 8·83	-0.23 -0.06	Me	8.05	-0.25				Me	<b>8</b> ∙38	-0.50	<b>8</b> ·19	0.00	7.81	0.54
(VIIIb) I	H	6.90	0.00	Me	8.26		Me	8.26		Me	8.47		8.33		7.90	
$(IXa)^m$	Ĥ	6.99	-0.07	Ĥ	4.49	-0.16	H	3.94	-0.20						7.89	0.44
(IXb) »	ਸ	6.80	0.04	ਸ	4.47	-0.25	H	3.96	-0.26						7.90	0.39
(IXc) °	Ĥ	6.83	5.01	Ĥ	4.48	0 10	H	3.99							7.90	

<sup>(1)</sup> T Values; solutions in CCl<sub>4</sub>.  $b \Delta = \tau(C_{6}H_{6}) - \tau(CCl_{4})$ . c Coupling constants: H-2,Me-2 6.85, H-2,H-3 10.0, H-3,Me-4 1.4, Me-4,H-5 ca. 0.9, H-5,Me-6 0.9-1.0 Hz. <math>d H-2,Me-2 6.8, H-2,H-3 9.8, H-3,Me-4 ca. 1.2, Me-4,H-5 not determined; H-5,Me-6 0.9-1.0 Hz. d H-2,Me-3 small, Me-3,Me-4 ca. 1.0, Me-4, H-5 small; H-5,Me-6 0.7-0.8 Hz. f H-2,Me-3 small, Me-3,H-4 1.4-1.5 Hz. d H-2,H-3 ca. 8, H-3,Me-4 ca. 1.5, Me-5,Me-6 ca. 1.5 Hz. d H-2,H-3 7.1, H-2,Me-4 ca. 1.2, H-2,Me-3 small, Me-3,H-4 1.4-1.5 Hz. d H-2,H-3 ca. 8, H-3,Me-4 ca. 1.5, Me-5,Me-6 ca. 1.5 Hz. d H-2,H-3 7.1, H-2,Me-4 ca. 1.2, H-2,Me-5 small, H-3,Me-4 ca. 1.2, Me-4,Me-5 small, Me-5,Me-6 ca. 1.5 Hz. d H-2,H-3 7.1, H-2,Me-4 ca. 1.2, H-2,Me-5 small, H-3,Me-4 ca. 1.2, Me-4,Me-5 small, Me-5,Me-6 1.5 Hz; CO<sub>2</sub>Me  $\tau$  6.40,  $\Delta$  0.26. d H-2,Me-2 7.0, H-2,Me-3 small, Me-3,H-4 1.4, H-4,Me-5,Me-6 ca. 1.5 Hz. d H-2,Me-3 small, Me-5,Me-6 ca. 1.6 Hz; CO<sub>2</sub>Me  $\tau$  6.36. m H-2,H-3 7.4, H-3,H-4 11.4 Hz. n Coupling as for (IXa); CO<sub>2</sub>Me  $\tau$  6.35,  $\Delta$  0.26. d C

All the amides also have an NH signal,  $\tau 3.88-4.10$  (d, J 7-8 Hz, or broad peak), a cyclohexyl methine signal,  $\tau 6.44-6.60$  br, and other cyclohexyl absorption underlying the  $\tau 8.0-9.2$  region.

does not have the structure (XIa) previously assigned with the help of early n.m.r. data.<sup>2,3</sup> In compound (XIa), which was assumed to arise by cyclohexylaminecatalysed deprotonation of (Ia) and reprotonation,\* both vinyl protons should be coupled to H-4 and give doublets (J ca. 8 Hz). In fact one vinyl proton (H-3) The u.v. spectra of our amides and esters are of little value in determining the position and stereochemistry

\* To test the possibility of easy and general base-catalysed isomerisations we heated amide (IVa) with excess of cyclohexylamine under much more vigorous conditions than those used in the photolyses. No isomerisation was detected.

the photolyses. No isomerisation was detected. <sup>12</sup> P. M. Collins and H. Hart, J. Chem. Soc. (C), 1967, 1197. of the double bonds, and empirical rules such as Woodward's are inappropriate. Multiple substitution of butadienes causes twisting, with irregularity in the positions and intensity of u.v. maxima, and ultimately in the complete loss of maxima in the 210-250 nm



region.<sup>13</sup> Table 2 shows this to be the case for all products except (IXa-c); analogous results have been reported 11,12 and discussed 12 previously. N.m.r. data for compounds (IXa-c) show the 3,4-double bond to have cis (Z) stereochemistry. When any coupling between methyls and protons on C-3 and C-4, or vice versa, was unambiguously determined, the value of |I| $(1.4-1.5 \text{ Hz})^*$  again supported 3Z-stereochemistry: allylic coupling constants are discussed later. Collins and Hart,<sup>12</sup> and Quinkert and his co-workers,<sup>6</sup> have shown that the initially formed 3Z-esters or amides undergo further photoisometisation to the 3E-isometis if light of sufficiently low wavelength is used. We found no evidence of secondary isomerisation under our conditions (Pyrex filter, and avoiding over-irradiation): this point was tested more closely in the preceding paper.<sup>4</sup>

The stereochemistry of the 5,6-bond in the photoproducts is of interest. Barton and Quinkert's original work<sup>2</sup> implied that one of the possible stereoisomeric photoproducts was formed predominantly. Our later studies 1,4 and others 11 confirm that the ring-opened products are formed with very high stereoselectivity: we have been unable to detect stereoisomers of the major products. Attempts to isomerise the 5,6-double bond by prolonged heating of selected amides with toluene-psulphonic acid or by over-irradiation (even through quartz) were unsuccessful. Since direct comparison of both 5,6-geometrical isomers was impossible we studied the n.m.r. spectra of amides in which the stereochemically dependent coupling between a 5-proton and 6-methyl

\* Coupling constants are corrected, when necessary, for the effects of imperfect resolution by use of the treatment in ref. 14, p. 313.

<sup>13</sup> W. F. Forbes, R. Shilton, and A. Balasubramanian, J. Org. Chem., 1964, 29, 3527.

<sup>14</sup> L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon, Oxford, 2nd edn., 1969.

<sup>15</sup> E. B. Whipple, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, 1960, **82**, 3010.

group could be identified and measured. The spectrum of (IIa) in carbon tetrachloride has two allylic methyl signals which overlap and are close to the third. Addition of  $[{}^{2}H_{6}]$  benzene to the solution causes selective solvent shifts (Table 3), allowing the peaks to be separated. A plot of peak positions against solvent composition allowed each peak to be identified. Optimum separation of the allylic methyls and the acetate peak was found in ca. 17% CCl<sub>4</sub>, 83% C<sub>6</sub>D<sub>6</sub>. Decoupling showed one of the methyl signals, assigned to the 6-methyl group, was significantly coupled only to the 5-vinyl proton, with |J| = 0.7 - 0.8 Hz.<sup>†</sup> The other allylic methyls gave quartets (|J| ca. 1.0 Hz), one of which (the 3-methyl) showed weak coupling to the 2-methylene group. Similar studies on (Ia), whose methyl peaks were separated in the spectrum of a solution in [2H<sub>6</sub>]benzene, showed a 5H,6Me coupling with |J| 0.9-1.0 Hz. It is normally found that trans allylic coupling in systems (XII), where Y does not contain a conjugated double bond, is smaller than *cis* (*i.e.*  $|J|_{trans} < |J|_{cis}$ ), a difference of about 0.6 Hz being general.<sup>15,16</sup> In 2-substituted propenes, *cis*-allylic coupling has J - 1.0 to -1.7 Hz, and trans coupling -0.4 to -1.2 Hz.<sup>15,16</sup> The closest analogues in the literature allow ranges to be given of  $|J|_{cis}$  1.4  $\pm$  0.2,  $|J|_{trans}$  0.75  $\pm$  0.2 Hz. Coupling in isopropenyl acetate has  $|J|_{cis}$  1.2,  $|J|_{trans}$  0.6 Hz,<sup>15</sup> and an extensive series of olefins used in juvenile hormone synthesis <sup>17</sup> have  $|J|_{trans}$  0.8 Hz. It appears from such considerations that compounds (Ia) and (IIa) have the 5-proton and 6-methyl trans (i.e. a 5E-configuration). Similar arguments apply to 5-methyl,6-methyl couplings, which have |I| 1.4 - 1.6 Hz (Table 3): literature values for trans- and cis-homoallylic coupling in enol acetates  $^{18,19}$  and close analogues  $^{20}$  are  $1\cdot 3-1\cdot 6$ , and  $1\cdot 0-$ 1.15 Hz, respectively.

It seemed desirable to develop other methods for determining the stereochemistry of enol acetates, since coupling constants do not always allow a decision to be made.<sup>21</sup> It is known that the signal of a  $\beta$ -vinyl proton *cis* to the oxygen function in enol ethers or enol acetates falls at lower field than that of the *trans* proton. This is true for solutions in carbon tetrachloride, 18, 19, 22 but the difference is enhanced in benzene solution,19,21 and it seemed that solvent shifts could be useful. Literature data for (XII and XIII; Y = OAc) were combined to

<sup>16</sup> M. Y. de Wolf and J. D. Baldeschweiler, J. Mol. Spectroscopy, 1964, 13, 344; E. B. Whipple, J. H. Goldstein, and G. R. McLure, J. Amer. Chem. Soc., 1960, 82, 3811; L. M. Jackman and R. H. Wiley, J. Chem. Soc., 1960, 2881; A. A. Bothner-By and H. Günther, Discuss. Faraday Soc., 1962, 34, 127.
<sup>17</sup> B. M. Trost, Accounts Chem. Res., 1970, 3, 120.
<sup>18</sup> W. E. Parham and J. F. Dooley, J. Org. Chem., 1968, 33, 1476.

1476.
<sup>19</sup> H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, J. Org. Chem., 1969, 34, 2324.
<sup>20</sup> H. Hecht and B. L. Victor, J. Amer. Chem. Soc., 1968, 90, 3333; N. S. Bhacca and R. K. Sharma, Tetrahedron, 1968, 24, 6319.

 <sup>21</sup> H. O. House and V. Kramar, J. Org. Chem., 1963, 28, 3362.
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<sup>&</sup>lt;sup>†</sup> There may be some small coupling between the 4- and 6methyl groups which results in line broadening. The decoupled 6-methyl peak had W1 2.0 Hz, cf. the sharp acetate peak, W1 1.0 Hz.

give  $\Delta[\tau(C_6H_6) - \tau(CCl_4)]$  values of  $0.10 \pm 0.03$  for the  $\beta$ -proton in cis-(XII),  $-0.05 \pm 0.06$  for that in trans-(XII),  $0.23 \pm 0.02$  for the  $\beta$ -methyl in *cis*-(XIII), and  $0.06 \pm 0.03$  for the  $\beta$ -methyl in trans-(XIII). For the acetate and  $\alpha$ -methyl groups,  $\Delta$  values are *ca*. 0.30 and 0.16 (one reliable value only).\* The  $\Delta$  values of 5substituents in the amides and esters (I-VIa) and (IVb) (Table 3) are consistent with a trans relationship with the 6-methyl group. Attempts to use the solvent shifts of the 4-substituents were unsuccessful, owing to the lack of analogues, but the large discrepancy between the  $\Delta$  values of the 4-protons in (IXa and b) and those in the other amides and esters is noteworthy. In (IXa, b, and c) the 6-acetoxy-group is forced to lie *cis* to the main chain.

To find whether other o-quinol esters would suffer stereoselective photochemical ring-opening we irradiated 6-benzoyloxy-2,4,6-trimethylcyclohexa-2,4-dienone.<sup>23</sup> In the presence of cyclohexylamine this gave a single amide (ca. 90% by g.l.c.), some 2,4,6-trimethylphenol, unchanged dienone, and a trace of unidentified material. The amide (XIVa) has n.m.r. chemical shifts which compare well with those of (Ia) when the change of acetate to benzoate is allowed for (by use of comparisons of the quinol acetate and benzoate spectra, and data for enol benzoates 24). The solvent shifts and coupling constants also agree well, suggesting 5E stereochemistry in this case also. This result is consistent with our finding that pentamethyl-o-quinol benzoate, on irradiation in ether, gives exo-6-benzoyloxy-1,3,4,5,6-pentamethylbicyclo[3,1,0]hex-3-en-2-one, analogous to the acetate described in the previous paper,<sup>4</sup> and the report that both 2,4,6-triphenyl-o-quinol acetate and benzoate give analogous bicyclohexenones via ketens.25

In addition to the irradiations described, quinol acetates (I)—(V) and (VII)—(X) and quinol benzoate (XIV) were irradiated in ether to detect any formation of bicyclohexenones or other products. In no case was a bicyclohexenone found. Each quinol acetate and compound (XIV) gave its parent phenol; compound (I) also gave 3-acetoxy-2,4,6-trimethylphenol as reported by Barton and Quinkert;<sup>2</sup> compound (XIV) gave some 3-benzoyloxy-2,4,6-trimethylphenol, and compound (II) gave 3-acetoxy-2,4,5-trimethylphenol in an analogous way. The keten from compound (V) was not trapped during irradiation in methanol, only 2,3,5,6-tetramethylphenol being detected. No keten could be trapped from the bicyclic quinol acetate (X), even by cyclohexylamine, and we believe that no keten was formed.

The stereoselectivity of the dienone-to-keten valence isomerisation has parallels in the opening of cyclobutenones.<sup>11</sup> Baldwin and his co-workers have in-

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vestigated the suggestion that the preferred groundstate conformation of the cyclic partner dictates the subsequent steps, but consider this explanation to predict the wrong stereochemistry in one cyclobutenone case.<sup>26</sup> The suggestion does, however, seem to have virtues for cyclohexadienone opening. Dreiding models show the dihedral angles between the C-3, C-4, C-5, C-6 plane and the 6-substituents in the dienone to be ca. (+) $90^{\circ}$  and ca. (-)  $20^{\circ}$ . Steric repulsions should be minimised by having the small<sup>21</sup> acetoxy-group in the 'equatorial' and the 6-methyl group in the 'axial' position. If the photoexcitation and collapse to keten occur so that the more ponderous 6-substituent † suffers minimum movement, the observed (5E) keten stereoisomer would be found. Ring-opening to give the 5Z-isomer would require the acetoxy-group to swing through an arc of ca. 160°, instead of ca. 20°; the methyl has to swing through ca. 90° in any case. The same explanation would fit the reported opening <sup>11</sup> of 2-chloro-4-methyl-3-phenylcyclobut-2-enone. Quinkert's group found 6-methyl-6-phenylcyclohexa-2,4-dienone to give comparable amounts of the 5E- and 5Z-ketens as kinetic products.<sup>6</sup> If one may assume the 6-phenyl group to occupy an 'axial' position in the dienone, it must swing through ca.  $90^{\circ}$  to reach the geometry of either keten: since its inertia is much higher than that of the 6-methyl, collapse to either keten should occur, with some preference for the Z-isomer (which involves methyl moving through  $20^{\circ}$  rather than  $160^{\circ}$ ).

If the stereoselectivity were to arise during the collapse of excited keten (or excited dienone) to ground state keten one might expect the proportions of 5E- and 5Z-isomers to reflect roughly their relative stabilities. Analogy with House and Kramar's equilibration studies on simple enol acetates <sup>21</sup> suggests a maximum preference of about 4:1, and that in favour of the 5Z-isomer. The observed preference for the 5*E*-product thus seems too great, and in the wrong sense to be explained by steric effects in the ground-state ketens or their immediate precursors. Clearly there are other stages at which stereoselectivity may arise, and we are investigating some of these.

#### EXPERIMENTAL

General experimental data are given in the first paper of this group. Most n.m.r. spectra were obtained with Perkin-Elmer or Varian HA 100 (100 MHz) instruments, or a Varian A60, with checks on the scale calibration. Decoupling experiments used the HA 100, or in one case a Perkin-Elmer R12B and Varian T60. Solvent-shift data were obtained from solutions of low and fixed concentration for compounds (Ia), (IIa), and (IVa), and of low but variable concentration for the other amides and esters: concentration effects appear to be insignificant.

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<sup>\*</sup> Errors in  $\tau$  values of vinyl protons may be appreciable if tetramethylsilane is used as internal standard and the instrument scale calibration is not checked. The ranges quoted refer to comparisons between spectra in single literature reports, where instrument errors have more chance of being constant. Errors for methyl signals will be smaller, and the ranges quoted include within- and between-report comparisons.

<sup>†</sup> The acetoxy-group has a moment of inertia 6-7 times greater than methyl.

6-Acetoxy-2,4,6-trimethylcyclohexa-2,4-dienone (I).-2,4,6-Trimethylphenol (12.0 g) in chloroform (90 ml) was added dropwise with stirring to a suspension of lead tetra-acetate (45 g) in chloroform (70 ml), with the temperature kept below  $30^{\circ}$ . After 2 h at  $25^{\circ}$  the mixture was shaken with water  $(3 \times 200 \text{ ml})$  and filtered through Celite, and the organic layer was dried (MgSO<sub>4</sub>) and evaporated. The oil crystallised from petroleum (b.p. 40-60°) to give the quinol acetate (I) (13.6 g, 88%), whose m.p., i.r., and u.v. spectra agree well with literature 27 data (see Table 1) (Found: C, 68·3; H, 7·5. Calc. for  $C_{11}H_{14}O_3$ : C, 68·0; H, 7·3%).

6-A cetoxy-3,4,6-trimethylcyclohexa-2,4-dienone (II).— 2,4,5-Trimethylphenol (12.0 g) was treated similarly. Distillation of the resultant oil (b.p. 96-100° at 0.6 mmHg), crystallisation from diethyl ether at  $-78^{\circ}$ , and washing of the crystals with cold petroleum (b.p.  $40-60^{\circ}$ ) gave the quinol acetate (II) (9.0 g, 60%) as lemon-yellow crystals (Found: C, 68.0; H, 7.1. C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> requires C, 68.0; H, 7.3%). This compound has been reported previously,<sup>28</sup> but not isolated or characterised.

6-Acetoxy-3,5,6-trimethylcyclohexa-2,4-dienone (III).— 2,3,5-Trimethylphenol (13.6 g), treated similarly, with distillation at 100-120° and 1 mmHg and crystallisation from diethyl ether at  $-78^{\circ}$  gave (III) as yellow crystals (6.95 g, 36%).

6-Acetoxy-4,5,6-trimethylcyclohexa-2,4-dienone (IV) — 2,3,4-Trimethylphenol (4·1 g) was treated with lead tetraacetate (15 g) as before. Distillation (b.p. 99-100° at 0.4 mmHg) and crystallisation from diethyl ether-petroleum (b.p. 40-60°) (1:3) mixture gave the quinol acetate (1.51 g, 26%), m.p. 62.5-64° (Found: C, 67.8; H, 7.3. C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> requires C, 68.0; H, 7.3%). The i.r. spectrum of this compound has been published 29 but its preparation has not apparently been reported.

6-Acetoxy-2,3,5,6-tetramethylcyclohexa-2,4-dienone (V).— 2,3,5,6-Tetramethylphenol (12.0 g) treated as in the preparation of compound (I), with crystallisation from petroleum (b.p. 30-40°), and silica-gel chromatography of the mother liquors, gave the quinol acetate (13.5 g, 81%), m.p. 60-61° (Found: C, 69.2; H, 7.8.  $C_{12}H_{16}O_3$  requires C, 69.2; H, 7.7%).

6-Acetoxy-4-bromo-2,3,5,6-tetramethylcyclohexa-2,4-dienone (VII).-4-Bromo-2,3,5,6-tetramethylphenol<sup>30</sup> (12.3 g) and lead tetra-acetate (35 g) treated similarly, with crystallisation from diethyl ether at  $-78^{\circ}$ , gave the quinol acetate (5·4 g, 35%), m.p. 88-90° (Found: C, 50·6; H, 5·1; Br,  $C_{12}H_{15}BrO_3$  requires C, 50.2; H, 5.3; Br, 28.3.27.9%).

6-Acetoxy-3,4,5,6-tetramethylcyclohexa-2,4-dienone (VIII). -2,3,4,5-Tetramethylphenol (1.19 g) (prepared by alkali fusion <sup>31</sup> of 2,3,4,5-tetramethylbenzenesulphonic acid <sup>32</sup>) and lead tetra-acetate (5.0 g) in chloroform, treated as in the preparation of (I), gave the quinol acetate (0.71 g, 43%) as lemon-yellow crystals, recrystallised from ether-petroleum (Found: C, 69.4; H, 7.7. C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> requires C, 69.2; H, 7.74%).

1-Acetoxybicyclo[4,3,0]nona-3,5-dien-2-one (IX) and 1-Acetoxybicyclo[4,4,0]deca-3,5-dien-2-one (X).-These were made by the published procedures.<sup>33</sup>

Irradiations in the Presence of Cyclohexylamine.-Each quinol acetate or quinol benzoate (1.0 g) in dry ether (50 ml)and cyclohexylamine (10 ml; redistilled) was irradiated with a Hanovia 450 W lamp, through Pyrex, in a nitrogen atmosphere, under reflux. Monitoring by g.l.c. (generally silicone E30 column at 190-200°) and u.v. spectroscopy showed reaction to be rapid, and complete in ca. 2 h, with formation of a single amide. Washing of the solution with N-hydrochloric acid  $(2 \times 200 \text{ ml})$  then water, drying (MgSO<sub>4</sub>), and evaporation gave an oil. Crystallisation from petroleum (b.p.  $40-60^{\circ}$ ) at  $-78^{\circ}$  gave the pure amides. Yields of crystalline amides, and of crude amides in some cases, and physical data are in Tables 2 and 3. All amides have the correct molecular weights (mass spectra) and analytical data (Table 2). 1-Acetoxybicyclo[4,4,0]deca-3,5-dien-2-one (X) gave 5,6,7,8-tetrahydro-1-naphthol, and no detectable amount of photoamide.

Irradiation in Alcohols.—The quinol acetate (0.10 g) in methanol or ethanol (100 ml) was irradiated as before. Analysis by g.l.c. showed the mixture to contain virtually pure ester [from (IV) and (VIII)] or ester together with 10-15% of indanol [from (IX)]. Evaporation gave an oil which was purified by distillation (IVb) or alumina chromatography (IXb and c), or used directly for spectroscopy (VIIIb). Comparison with the crude products showed no decomposition to occur during purification.

Attempted Isomerisation of Amide (IVa) with Cyclohexylamine.—The amide (50 mg) in benzene (5 ml) and cyclohexylamine (480 mg, 30 mol. equiv.) was heated under reflux for 8 h. After work-up as before, gl.c. and n.m.r. analysis of the crude product showed no change.

6-Benzoyloxy-2,3,4,5,6-pentamethylcyclohexa-2,4-dienone. -Pentamethylphenol (2.46 g) in dry ether (50 ml) was heated under reflux with sodium hydride (0.36 g), with stirring for 6 h. The suspension of the sodium phenoxide was cooled to  $-20^{\circ}$ , recrystallised benzoyl peroxide (3.63 g) in dry ether (150 ml) was added dropwise with stirring, and the mixture was stirred for 0.5 h at  $-20^{\circ}$ . After a further 0.5h at 0°, and warming to 25° the product was added to icewater, and the ether layer was washed (NaHCO<sub>3</sub> solution then acidified  $FeSO_4$  solution and water) and dried (MgSO<sub>4</sub>). Evaporation gave a yellow oil (2.82 g) which contained quinol benzoate, pentamethylphenol, and benzoyl peroxide. Chromatography on alumina, followed by crystallisation from petroleum (b.p. 40-60°) gave the cyclohexadienone (0.56 g, 20%) as pale yellow crystals, m.p. 120-122° (Found: C, 75.8; H, 7.2. C<sub>18</sub>H<sub>20</sub>O<sub>3</sub> requires C, 76.0; H, 7.0%),  $\lambda_{max.}$  233, 274, 282, and 321 nm (log  $\varepsilon$  4.15, 3.37, 3.36, and 3.63),  $\nu_{max.}$  1725, 1670, and 1640 cm<sup>-1</sup>,  $\tau$  1.95 (m) and 2.58 (m) (Ph), 7.93 (3-Me), 8.10 (2- and 4-Me), 8.23 (5-Me), and 8.62 (6-Me), assigned on the basis of chemical shift and solvent shift analogy with the quinol acetate.<sup>4</sup>

Irradiation of 6-Benzoyloxy-2,3,4,5,6-pentamethylcyclohexa-2,4-dienone.—(a) In wet ether. The dienone (1.0 g) in ether (200 ml) saturated with water was irradiated through Pyrex until the 321 nm absorption had decreased to a constant intensity. Drying and evaporation gave a yellow oil (ca. 1.0 g) containing one major component and 7-8 minor ones, including pentamethylphenol and unchanged quinol benzoate. Chromatography on Florisil (twice) gave the

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photoproduct (250 mg from 700 mg) 90% pure; crystallisation from n-pentane at  $-78^{\circ}$  then gave exo-6-benzoyloxy-1,3,4,5,6-pentamethylbicyclo[3,1,0]hex-3-en-2-one, m.p. 57— 59° (Found: C, 75·8; H, 7·0. C<sub>18</sub>H<sub>20</sub>O<sub>3</sub> requires C, 76·0; H, 7·0%),  $\nu_{max}$  1725, 1700, and 1640 cm<sup>-1</sup>,  $\lambda_{max}$  203, 233, 265, and 325 nm (log  $\varepsilon$  4·37, 4·51, 3·92, and 2·87),  $\tau$  2·01 (m), and 2·54 (m) (Ph), 7·91 (q, J 1·2 Hz, 4-Me), 8·37 (q, J 1·2 Hz, 3-Me), 8·58 (6-Me), 8·72 (5-Me), and 8·79 (1-Me); spectra similar to those of the 6-acetoxy-analogue.<sup>4</sup>

(b) With cyclohexylamine. The quinol benzoate (0.10 g) in ether (10 ml) and cyclohexylamine (0.36 g) was irradiated for 1 h through Pyrex. Washing with 0.01N-hydrochloric acid (to remove cyclohexylamine) then water, drying (MgSO<sub>4</sub>), and evaporation gave a pale yellow oil (0.115 g). Chromatography on Florisil gave 95% pure N-cyclohexyl-6-benzoyloxy-2,3,4,5-tetramethylhepta-3,5-dienamide,  $v_{max}$ .

3380 (NH), 1760, and 1670 cm<sup>-1</sup>,  $\lambda_{max}$  209, 231, 275, and 283 nm, as a colourless oil (63 mg),  $\tau$  1.81 and 2.43 (aromatic multiplets), 3.55br (NH), 6.36br (cyclohexyl methine), 6.78 (q, J 7 Hz, H-2), 8.14 (q, J 1.6 Hz, 6-Me), 8.23, (s, 3- and 4-Me), 8.40 (q, J 1.6Hz, 5-Me), and 8.88 (d, J 7Hz, 2-Me). As in the spectra of some of the other amides from 2methyl quinol acetates, the 2-methyl doublet shows a small subsidiary doublet owing, we believe, to internal rotation in an unsymmetrical environment.

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