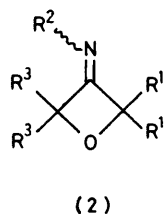
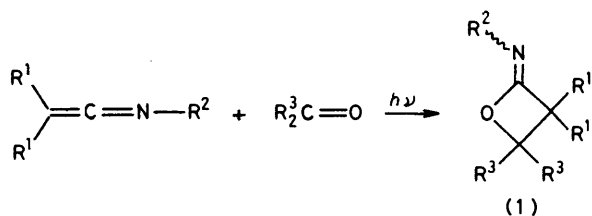


## Photocycloadditions of *p*-Quinones to Ketenimines

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Photo-induced cycloadditions of *p*-benzoquinone derivatives and 1,4-naphthoquinone to several ketenimines afforded 1 : 1 adducts. Two consecutive adducts, 2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-ones and 1-aza-spiro[3.5]nona-5,8-diene-2,7-diones, were obtained from these photolyses in moderate yields. Their structures, which had been postulated as intermediates in a similar reaction, were determined by physical and chemical methods. These two types of spiro-cyclohexa-2,5-dienone gave the rearranged products, 2,3-dihydro-5-hydroxybenzofuran-2-imines and 5-hydroxyindolin-2-ones, respectively, by Lewis-acid catalysed rearrangement.

In recent years, several reports have appeared on the thermal and photo-induced cycloadditions of aldehydes,



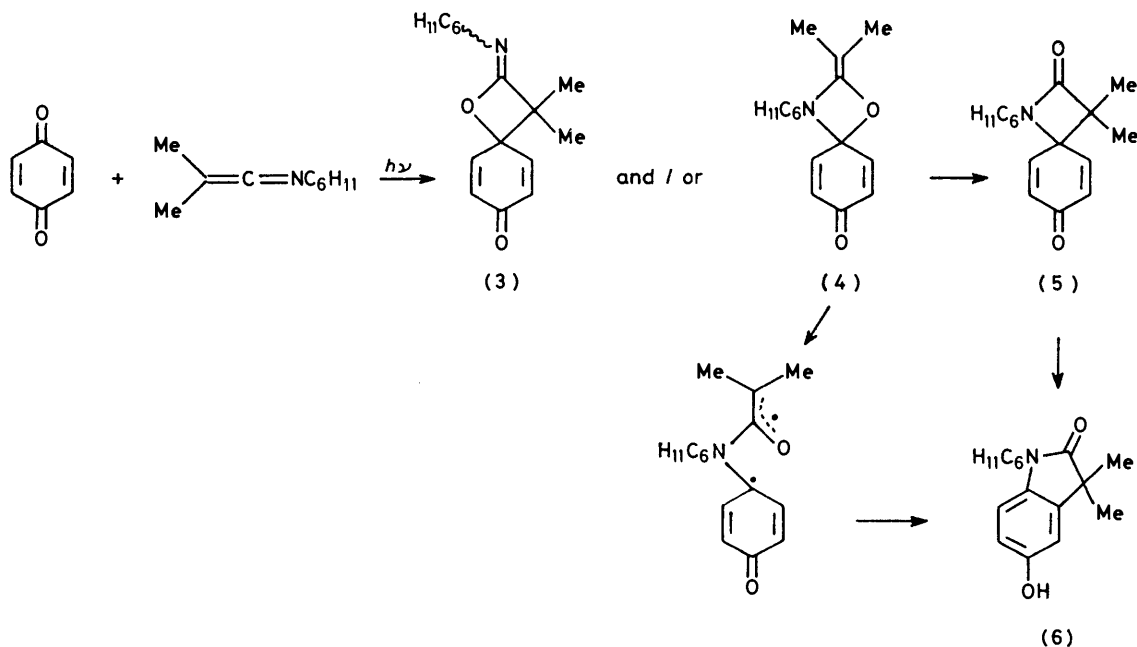
ketones, and thioketones to form 2-imino-oxetans (1), 3-imino-oxetans (2), and 2-iminothietans.<sup>1,2</sup> In (2 + 2)-

cycloadditions of the carbonyl function in *p*-quinonoid systems, Staudinger<sup>3</sup> and Martin and his co-workers<sup>4</sup> reported that *p*-benzoquinone reacts thermally with ketens to give spiro-β-lactones, and Bryce-Smith and Gilbert<sup>5</sup> reported a synthesis of oxetans involving the photo-induced cycloadditions of *p*-quinone to olefins.

Ishibe and Yamaguchi<sup>6</sup> found that (*N*-cyclohexyl)-dimethylketenimine, on photoreaction with *p*-benzoquinone or 1,4-naphthoquinone, forms the 1 : 1 adducts, 1-cyclohexyl-5-hydroxyindolin-2-one derivatives (6). They postulated the reaction mechanism in Scheme 1, with the heterocyclic spiro-cyclohexa-2,5-dienones (3)–(5) as possible intermediates for the formation of the products (6) and preferred the photoaddition of *p*-quinones across the C=N double bond of ketenimine as the primary reaction (Scheme 1).

We recently reported<sup>7,8</sup> the interesting results of reactions of 1-oxaspiro- and 1-azaspiro-[3.5]nona-5,8-diene-2,7-diones with nucleophiles, an extension of the synthesis of heterocyclic spiro-cyclohexa-2,5-dienones. Cyclohexadienone derivatives are useful synthetic precursors in organic and natural products chemistry.<sup>9</sup>

We report here the isolation of substituted 2-imino-1-



SCHEME 1

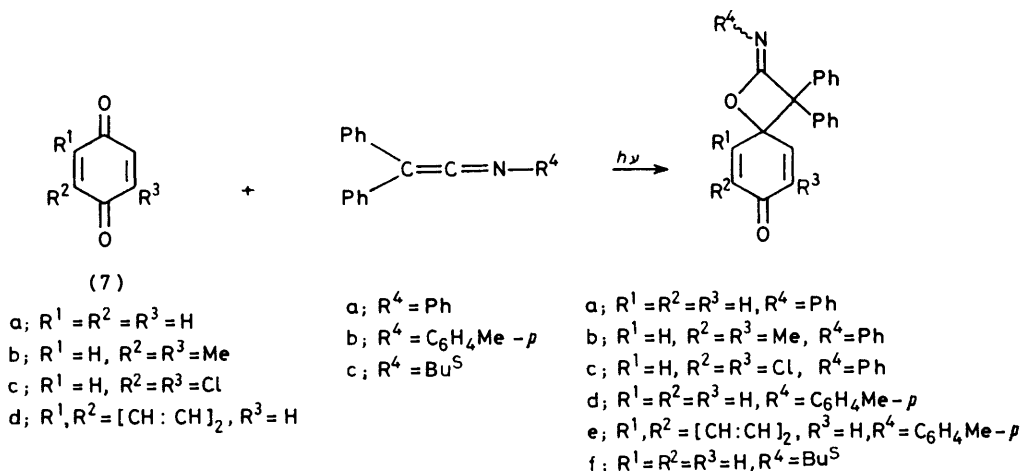
oxaspiro[3.5]nona-5,8-dien-7-ones (9) and (16) and substituted 1-azaspiro[3.5]nona-5,8-diene-2,7-diones (11) and (17), which were proposed as intermediates by Ishibe and Yamaguchi,<sup>6</sup> and the Lewis-acid catalysed rearrangement of these products.

#### RESULTS

Photoreactions of benzene solutions of *p*-quinones (7) and ketenimines (8) and (15) were carried out in a hard glass vessel by external irradiation with a high-pressure mercury lamp. The reactions were followed by t.l.c. After several hours irradiation, the photoadducts were isolated by direct crystallisation from the reaction mixtures, without contact with any Lewis acids. Attempts to isolate the photo-products from the reaction mixtures by chromatography on silica gel or alumina led to the rearranged products (see below).

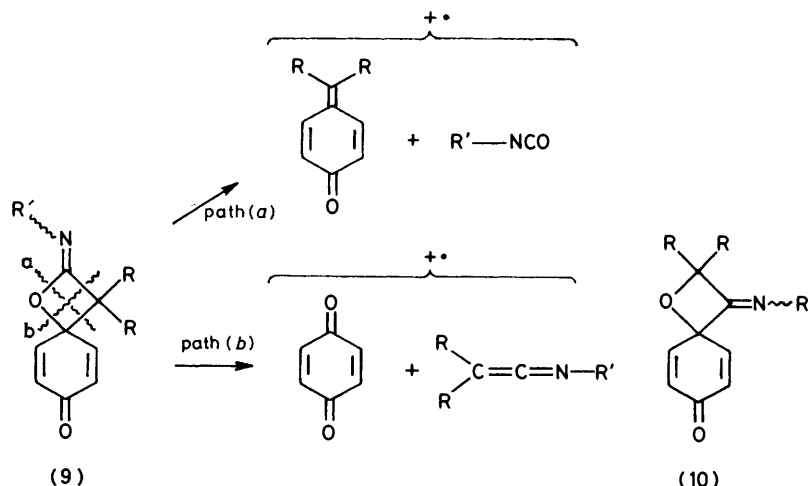
showed cyclohexa-2,5-dienone ring protons at  $\delta$  6.3—7.2 p.p.m. as AA'BB' quartets. These spectral data are quite different from those of the 5-hydroxyindolin-2-one derivatives isolated by Ishibe and Yamaguchi.<sup>6</sup> The photo-products appear to be formed by cycloaddition of the carbonyl function of *p*-quinones across the C=C double bond of ketenimines. Ishibe and Yamaguchi suggested that the photoadditions of *p*-quinone carbonyl groups across the C=N double bond of ketenimines is the initial reaction for the formation of 2-indolinones (Scheme 1), but this type of photoadduct [*i.e.* (4)] was ruled out by the spectroscopic evidence.

Singer and Bartlett<sup>10</sup> showed that the photo-induced cycloadditions of aromatic aldehydes and ketones to ketenimines afforded two different types of oxetans, *i.e.* 2-imino- (1) and 3-imino-oxetans (2). In the present study, there is a similar possibility for both spiro-2-imino- (9) and spiro-3-imino-oxetan (10) formation. The photoadducts



*Photoreactions of p-Quinones (7) with N-Substituted Diphenylketenimines (8).*—The i.r. spectra of the isolated photoproducts, which were shown to be 1:1 adducts of *p*-quinones and diphenylketenimines on the basis of elemental analyses and mass spectra, exhibited strong imino-bands at 1730—1740  $cm^{-1}$  and strong conjugated carbonyl bands at 1650—1695  $cm^{-1}$ . The n.m.r. spectra

were identified as 2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-ones (9) on the basis of mass-spectral cleavage patterns, which ruled out the spiro-3-imino-oxetan structures (10). All the ions detected were *p*-quinone diphenylmethide and ketenimine fragments from path (a) and path (b) cleavages (Scheme 2) which can arise only from the 2-imino-spiro-oxetans (9) and not from (10).



SCHEME 2

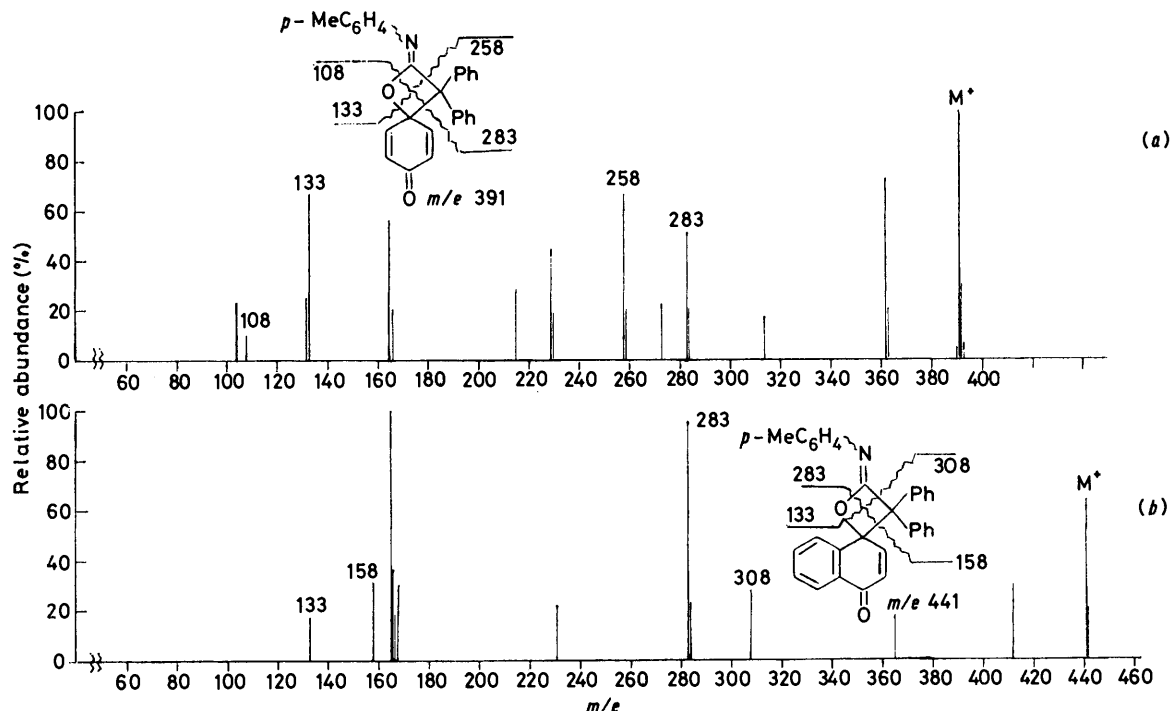
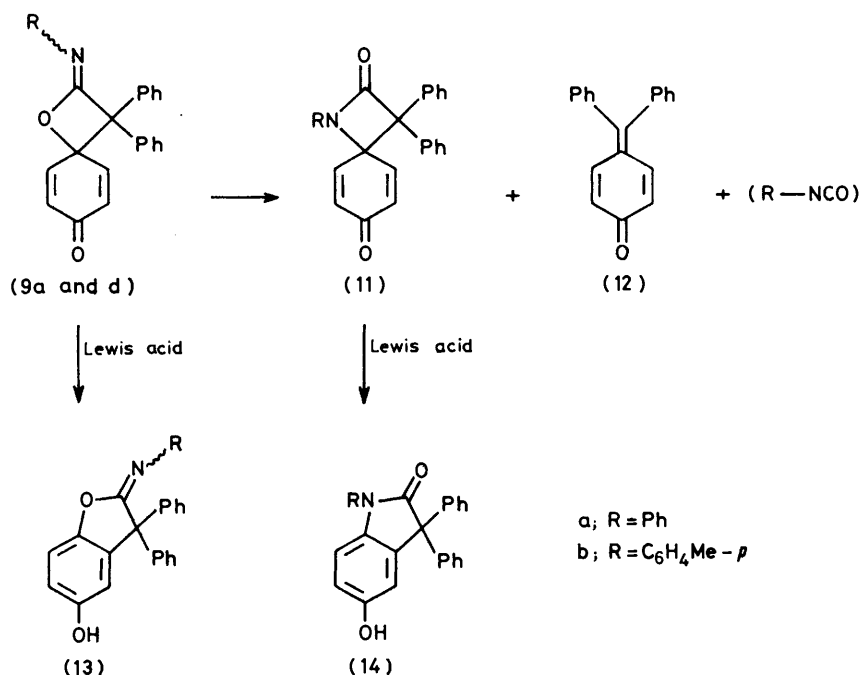


FIGURE 1 (a) The mass spectrum of the photoadduct of *p*-benzoquinone and diphenyl-(*N*-*p*-tolyl)ketenimine. (b) The mass spectrum of the photoadduct of 1,4-naphthoquinone and diphenyl-(*N*-*p*-tolyl)ketenimine

There was no detectable adduct formation in the dark in any of the systems studied. The results of the photoadditions of (7) to (8) are shown in Table 1 and their spectroscopic data are presented in Table 2.

in Table 1 are lower limits of the extent of cycloaddition. 2,3-Dihydro-5-hydroxybenzofuran-2-imine (13) and 5-hydroxyindolin-2-one (14) were obtained [instead of (9)] by silica gel chromatography of the photoreaction mixture of



The photoadducts were all isolated by direct crystallisation from the reaction mixtures. The relatively low yields were partially due to further subsequent photo-reaction of the 2-imino-spiro-oxetans (9), so the yields given

(7a) and (8a) after 24 h irradiation. Compound (13b) appeared to be formed from (9d) by silica-gel-catalysed rearrangement, since it was obtained in a quantitative yield by passing (9d), in benzene, through a silica gel column. It

TABLE 1

Photocycloadditions of *p*-quinones (7) to diphenyl-*N*-substituted-ketenimines (8)

<i>p</i> -Quinone	Ketenimine	Molar ratio (7) : (8)	Irradiation time/h	Product	Yield (%)
(7a)	(8a)	0.67	3	(9a)	47
(7b)	(8a)	0.67	3	(9b)	3
(7c)	(8a)	0.67	7	(9c)	9
(7a)	(8b)	2.00	2	(9d)	23
(7a)	(8b)	0.50	7	(9d)	35
(7a)	(8b)	0.67	24	(13b) + (14b)*	27 + 42 *
(7d)	(8b)	1.50	7	(9e)	48
(7a)	(8c)	1.00	3	(9f)	5

\* T.l.c. separation.

TABLE 2

Spectroscopic data for the photoadducts (9a—f) \*

Photo-adduct	M.p. (°C)	I.r. <sup>a</sup> (cm <sup>-1</sup> )	<sup>1</sup> H N.m.r. <sup>b</sup>
(9a)	132—134	1 735, 1 680	6.38 (2 H, d, <i>J</i> 11), 6.78 (2 H, d, <i>J</i> 11), 7.3—7.6 (10 H, m), 7.7—7.9 (5 H, m).
(9b)	123—124	1 730, 1 650	1.84 (6 H, s), 6.39 (2 H, s), 7.1—7.7 (10 H, m), 7.5—7.7 (5 H, m).
(9c)	124—126	1 740, 1 695	6.90 (2 H, s), 7.3—7.5 (10 H, m), 7.6—7.9 (5 H, m).
(9d)	134—135	1 740, 1 680	2.35 (3 H, s), 6.23 (2 H, d, <i>J</i> 10), 6.73 (2 H, d, <i>J</i> 10), 7.2—7.8 (14 H, m).
(9e)	149—150	1 735, 1 670	2.36 (3 H, s), 6.35 (1 H, d, <i>J</i> 10), 6.82 (1 H, d, <i>J</i> 10), 6.9—8.2 (18 H, m).
(9f)	101—102	1 740, 1 670	0.9—1.8 (8 H, m), 3.8—4.2 (1 H, m), 6.26 (2 H, d, <i>J</i> 10), 6.73 (2 H, d, <i>J</i> 10), 7.1—7.8 (10 H, m).

<sup>a</sup> KBr disc. <sup>b</sup> In CDCl<sub>3</sub>, p.p.m. from SiMe<sub>4</sub>; *J* in Hz.

was also produced from (9d) by boron trifluoride-ether (1:1)-catalysed isomerisation in 90% yield. On the other hand (14b) was a subsequent photoreaction product, because irradiation of the isolated spiro-oxetan-2-imine (9d) in benzene for 24 h gave it in 50% yield. It is, however, difficult to explain the photorearrangement of (9d) directly to (14b), which is similar to (6), reported by Ishibe and Yamaguchi,<sup>6</sup> so we examined the photoreaction of the isolated spiro-oxetan-2-imine (9a) to clarify it. Crystallisation of the reaction mixture after 24 h irradiation afforded the *p*-quinone diphenylmethide (12), m.p. 165—167 °C (lit.,<sup>3</sup> 167—168 °C) in a low yield, along with colourless crystals, m.p. 124—126 °C, also in very poor yield. Spectroscopic data of this compound [i.r. (KBr) 1 750 and 1 670 cm<sup>-1</sup>; n.m.r. δ 6.50 (2 H, d, *J* 10 Hz), 6.81 (2 H, d, *J* 10 Hz), and 7.18—7.83 (10 H, m)] show it to be 1,3,3-triphenyl-1-azaspiro[3.5]nona-5,8-diene-2,7-dione (11a), confirmed by an independent synthesis of (11a) and comparison of the m.p. and i.r. and n.m.r. spectra of this authentic sample with those of the photo-isomerised product from (9a). This authentic sample of (11a) was prepared by (2 + 2)cycloaddition of 4-(phenylimino)cyclohexa-2,5-dienone with diphenylketen in benzene at 0 °C.

The synthesised spiro-β-lactam (14a) was treated with boron trifluoride-ether(1:1) in benzene to yield a 5-hydroxyindolin-2-one derivative, as in the rearrangements of cyclohexadienones to phenol derivatives.<sup>11</sup> This compound had the same spectroscopic properties as the photoreaction product (14a) of *p*-benzoquinone and (8a) isolated by silica gel t.l.c.

These observations suggest that the spiro-oxetan-2-imines (9) and the subsequent photo-isomerised spiro-β-lactams (11) are stable isolable materials, and that their spiro-cyclohexa-2,5-dienones gave the rearrangement products by silica-gel catalysis.

**Photoreactions of *p*-Benzoquinone (7a) with *N*-Substituted Dimethylketenimines (15).**—The photo-induced cycloadditions of *p*-benzoquinone (7a) to *N*-substituted dimethylketenimines (15a—c) were not essentially different from those of (7a) to diphenylketenimines (8). The photoadducts were isolated by direct crystallisation from the reaction mixtures. The structures were assigned by the spectroscopic analyses and in some cases by the independent synthesis of an authentic sample. The difference between the photoreactions of (7a) with (8) and with (15) lies in the photo-sensitivity of the initial photoadducts; *i.e.* the 3,3-dimethylspiro-compounds (16) and the 3,3-diphenylspiro-derivatives (9). The adduct (9a) was partially decomposed to (11) and (12) after 15 h irradiation, whereas after a short irradiation (1.5 h) of the benzene solutions of (7a) + (15), the adducts (16) could be isolated by direct crystallisation from the reaction mixtures. But after a longer irradiation (7 h), the adducts (16) gave the photo-isomerised products, 3,3-dimethyl-1-azaspiro[3.5]nona-5,8-diene-2,7-diones (17), isolated by direct crystallisation or by t.l.c. on silica gel.

These results are set out in Tables 3 and 4.

TABLE 3

Photocycloadditions of *p*-benzoquinone (7a) to dimethyl-*N*-substituted-ketenimines (15)

Ketenimine	Molar ratio (7a) : (15)	Irradiation time/h	Product	Yield (%)
(15a)	1 : 1	1.5	(16a)	5
(15a)	1 : 1	7	(17a)	10
(15b)	1 : 1	7	(17b)	10
(15c)	1.5 : 1	1.5	(16c)	25
(15c)	1 : 1	7	(17c)	9
(15c)	1 : 1	20	(18c) *	14 *

\* T.l.c. separation.

TABLE 4

Spectroscopic data for the photoadducts (16) and (17)

Photo-adduct	M.p. (°C)	I.r. (cm <sup>-1</sup> )	<sup>1</sup> H N.m.r.*
(16a)	112—114	1 735, 1 680	1.45 (6 H, s), 6.35 (2 H, d, <i>J</i> 11), 7.17 (2 H, d, <i>J</i> 11), 7.27 (5 H, br s).
(17a)	156—157	1 760, 1 745, 1 665	1.38 (6 H, s), 6.50 (2 H, d, <i>J</i> 10), 7.10 (2 H, d, <i>J</i> 10), 7.2—7.3 (5 H, m).
(17b)	154—157	1 755, 1 670	1.38 (6 H, s), 2.29 (3 H, s), 6.53 (2 H, d, <i>J</i> 10), 7.08 (2 H, d, <i>J</i> 5), 7.13 (2 H, d, <i>J</i> 10), 7.24 (2 H, d, <i>J</i> 5).
(16c)	112—113	1 750, 1 675	1.35 (6 H, s), 1.63 (6 H, s), 6.16 (2 H, d, <i>J</i> 10), 7.03 (2 H, d, <i>J</i> 10).
(17c)	90—92	1 760, 1 670	1.29 (6 H, s), 1.70 (6 H, s), 6.38 (2 H, d, <i>J</i> 10), 7.03 (2 H, d, <i>J</i> 10).

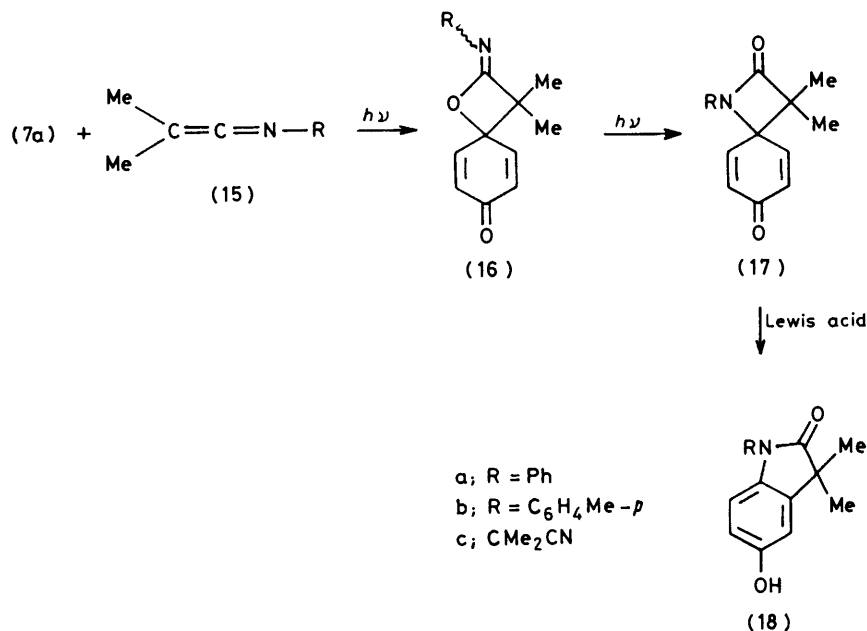
\* In CDCl<sub>3</sub>, p.p.m. from SiMe<sub>4</sub>; *J* in Hz.

Both the photoproducts (16) and (17) retain the cyclohexa-2,5-dienone moiety in their structures, as shown by their n.m.r. spectra. The i.r. spectra of the spiro-oxetan-2-imines (16a and c) show strong imino-oxetan bands at 1 735—1 750 cm<sup>-1</sup>. The isomeric spiro-β-lactams (17a—c) exhibited strong carbonyl bands at 1 755—1 760 cm<sup>-1</sup>, which were relatively stronger than those of the imino-

oxetan bands of (16). The mass spectra of (16) were also different from (17), as shown in Figure 2.

An authentic sample of (17a) was prepared by the cycloaddition of 4-(phenylimino)cyclohexa-2,5-dienone with

(17a) gave 3,3-dimethyl-5-hydroxyindolin-2-one, in an analogous cyclohexadienone-phenol molecular migration,<sup>11</sup> which exhibited the same spectroscopic properties as the photoproduct (18a), obtained by 7 h irradiation of (7a)



dimethylketen. All the physical properties [m.p., i.r., and n.m.r. spectra] of this compound were compared with those of the photoproduct (17a) and were found to be identical.

Lewis-acid-catalysed rearrangement of the synthesised

(17a) and then isolation by t.l.c. or separation on silica gel. Analogous compounds (18) were reported as photoadducts of (6) by Ishibe and Yamaguchi after chromatographic separation of the reaction mixtures.<sup>6</sup> Thus, these

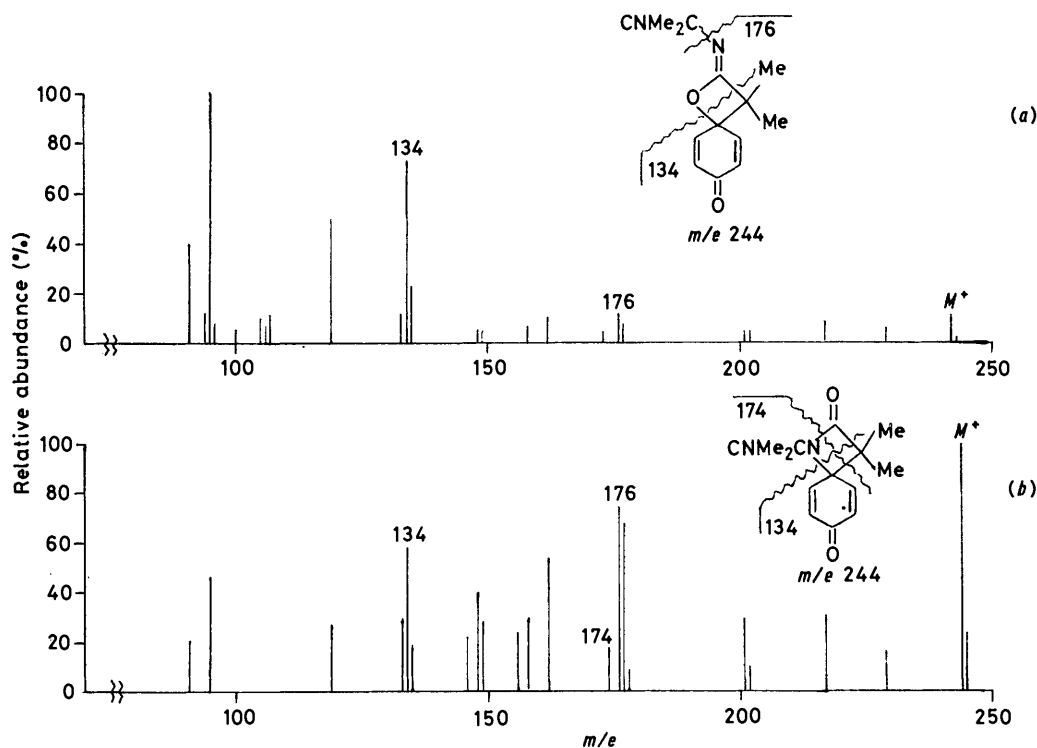


FIGURE 2 (a) The mass spectrum of the photoadduct of *p*-benzoquinone and (15c). (b) The mass spectrum of the photo-isomerised adduct of *p*-benzoquinone and (15c)

products are also derived from subsequent rearrangements of the initial products (17), catalysed by silica gel.

#### DISCUSSION

The similar patterns of photoadduct formations of ketenimines suggest that the  $n,\pi^*$  triplets of the carbonyl compounds are involved in the photocycloaddition reactions.<sup>12</sup> The photoaddition of fluorenone to ketenimines proceeds by way of a singlet fluorenone-ketenimine complex as well as by a triplet fluorenone addition.<sup>13</sup> Wilson and his co-workers<sup>14</sup> postulated triplet carbonyl-olefin charge-transfer complexes in the transition states of *p*-benzoquinone-ethylene systems instead of diradical processes.<sup>15</sup> Consequently, excited carbonyl functions of *p*-quinones add to ground-state ketenimines to form the initial photoadducts (9) and (16) across the C=C double bond of ketenimines. Both 2-amino- and 3-imino-oxetans were observed in the photocycloadditions of aromatic aldehydes and ketones with ketenimines.<sup>10,12</sup> However, Singer and Davis<sup>12,13</sup> found that

Substituents on the nitrogen atoms of (9) or (16) have no effect on the rate of these photoisomerisations. Under our experimental conditions the photo-excitation should occur on the carbonyl function of the cyclohexadienone moiety of the initial adducts (9) and (16), but in fact excitation causes cleavage of the carbon-oxygen bonds in the oxetan-2-imine rings to yield the diradical (19). These diradicals (19) formed from (9) and (16) should undergo one of two competitive paths, affording either the re-closed spiro- $\beta$ -lactams [(11) and (17)] by nitrogen-carbon bond formation or the *p*-quinone methides and isocyanate by carbon-carbon bond cleavage. *p*-Quinone diphenylmethide (12), a photo-decomposition product from (9) was stable under these conditions and isolable from the reaction mixtures. However, we could not isolate *p*-quinone dimethylmethide by the decomposition of (16). The initial photoadducts [(9) and (16)] and the subsequent photo-isomerised compounds [(11) and (17)] gave, by Lewis-acid catalysis, the rearranged products 2,3-dihydro-5-hydroxybenzofuran-2-imine (13),

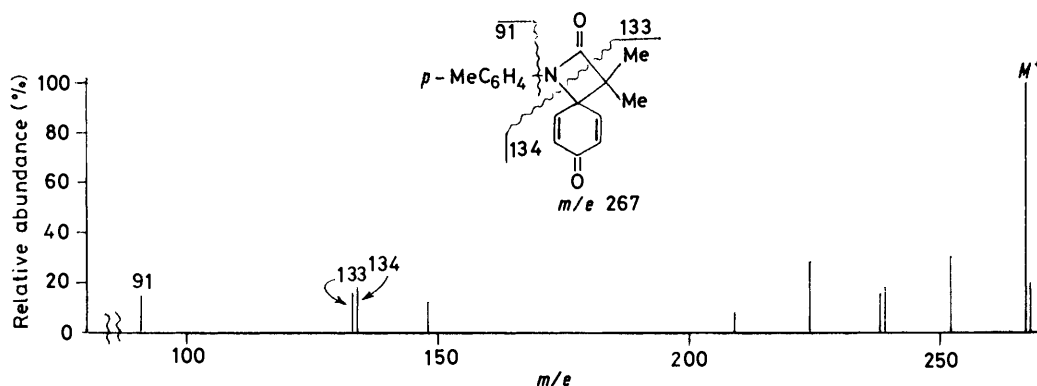


FIGURE 3 Mass spectrum of the photoadduct of *p*-benzoquinone and dimethyl(*N*-*p*-tolyl)ketenimine

photocycloadditions of fluorenone to both alkyl- and aryl-substituted ketenimines gave exclusively the 2-imino-oxetan; this is presumably the result of dipolar orienting influences in these fast photocycloadditions. Similar observations<sup>2</sup> were obtained in the photo-reactions of thioketone-ketenimine systems. The configuration (*syn* or *anti*) of the *N*-substituents of the spiro-oxetan-2-imines (9) and (16) was not established, but the n.m.r. spectra of (9d) and (16c) showed only a sharp singlet for the methyl groups associated with the nitrogen.

The subsequent photo-isomerisation of the spiro-oxetan-2-imines (9) and (16) to the spiro- $\beta$ -lactams (11) and (17) was the first example in photoreactions of 2-imino-oxetan systems. A similar photo-induced isomerisation was found in 2-imino-thietan systems.<sup>2</sup> In addition, several of the fluorenone-ketenimine adducts having *N*-phenyl substituents rearrange to  $\beta$ -lactams during chromatography, or by treatment of these adducts with lithium perchlorate in acetonitrile.<sup>12,13</sup> We found that the 3,3-dimethyl-spiro-cyclohexa-2,5-dienones (16) were more readily isomerised than the 3,3-diphenyl adducts (9) by irradiation (although we did not measure the relative rates), a fact which we are unable to explain.

and the 5-hydroxyindolin-2-one derivatives [(14) and (18)], respectively.

From these observations Scheme 3 may be formulated for these photocycloaddition reactions of *p*-quinonoids to ketenimines.

The photochemical reactions of *p*-quinonoids and ketenimines may thus produce new types of heterocyclic compounds, especially spiro-cyclohexadienones, and also be used for the synthesis of dihydrobenzofuran-2-imines and indolin-2-ones.

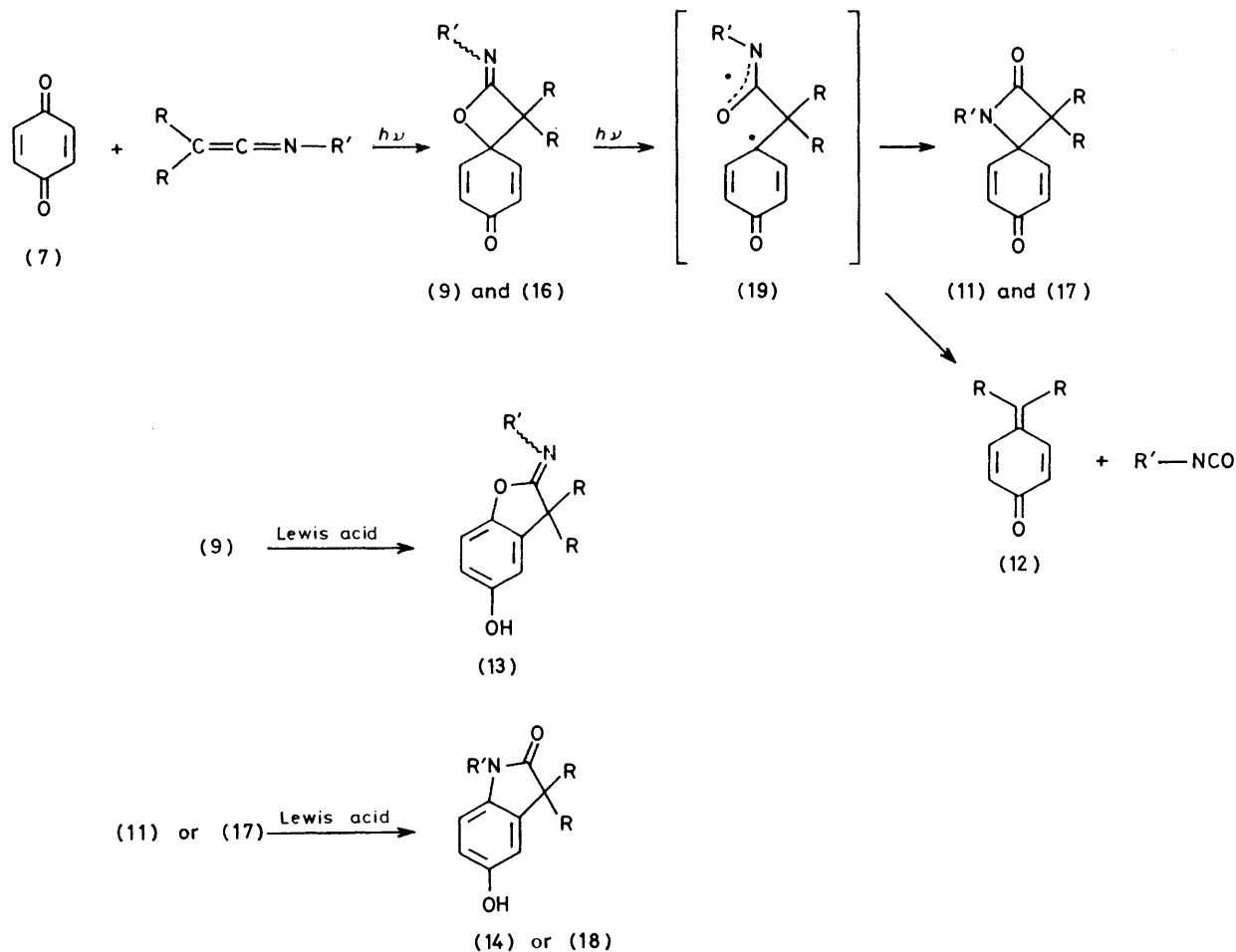
#### EXPERIMENTAL

**Materials.**—Commercially available *p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, and 1,4-naphthoquinone were purified by recrystallisation. 2,6-Dimethyl-*p*-benzoquinone was prepared by oxidation of 2,6-dimethylphenol with potassium nitrosodisulphonate.<sup>16</sup> Keteneimines (8a—c) and (15a—b) were prepared according to the literature.<sup>17</sup> Dimethyl-*N*-(2-cyanopropyl)ketenimine (15c) was obtained by the photochemical decomposition of 2,2-azobis(isobutyronitrile).<sup>18</sup> Solvents used were purified by standard distillation procedures. Chemical shifts are from SiMe<sub>4</sub>.

*General Procedure for Photoreactions of p-Quinones (7) and*

*Ketenimines* (8 and 15).—Nitrogen-purged hard-glass vessels containing benzene solutions (0.02–0.1M) of *p*-quinones (7) and the ketenimines (8) or (15) were irradiated with an external high-pressure mercury lamp at room temperature (for irradiation times see Tables 1 and 3). The reactions in each case were followed by t.l.c. After irradiation, the solvent was removed *in vacuo*, and the adducts were isolated by crystallisation of the crude product from ether–light petroleum (4:1). The isolated photoadducts [(9), (16), and (17)] were recrystallised from dichloromethane–light petroleum (yields and physical

*p*-tolyl)ketenimine (8b) or dimethyl-*N*-(2-cyanopropyl)-ketenimine (15c) were carried out by t.l.c. on Kieselgel GF<sub>254</sub> (Type 60, Merck) with elution with chloroform. After the usual work-up, products were obtained as crystals which were recrystallised from chloroform–*n*-hexane. Two products ( $R_F$  0.5 and 0.3) were obtained from the reaction of (7a) with (8a). The furan-2-imine (13b) ( $R_F$  0.5) is a colourless solid; m.p. 206–208 °C;  $\nu$ (KBr disk) 3 150, 1 695, 1 500, and 1 465  $\text{cm}^{-1}$ ;  $\delta$ (CDCl<sub>3</sub>) 2.35 (3 H, s), 6.6–7.0 (3 H, m), 7.17 (4 H, s), and 7.35 (10 H, s) (Found: C, 83.1; H, 5.7; N, 3.6. C<sub>27</sub>H<sub>21</sub>NO<sub>2</sub> requires C, 82.9; H, 5.4; N, 3.6%).



SCHEME 3

properties are shown in Tables 1–3. [For (9a): Found: C, 82.3; H, 4.9; N, 3.8. C<sub>26</sub>H<sub>19</sub>NO<sub>2</sub> requires C, 82.8; H, 5.0; N, 3.7%. For (9d): Found: C, 82.5; H, 5.7; N, 3.5. C<sub>27</sub>H<sub>21</sub>NO<sub>2</sub> requires C, 82.9; H, 5.4; N, 3.6%. For (16c): Found: C, 68.7; H, 6.6; N, 11.3. C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> requires C, 68.9; H, 6.6; N, 11.5%. For the spiro-β-lactam (17a): Found: C, 75.5; H, 6.1; N, 5.5. C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub> requires C, 75.9; H, 6.0; N, 5.5%.]

Other isolated photoadducts were checked by mass-spectrometric molecular-weight analysis as shown in Figures 2–4.

*Isolation of 2,3-Dihydro-5-hydroxybenzofuran-2-imine* (13b) and *5-Hydroxyindolin-2-one Derivatives* [(14b) and (18c)] by T.L.C.—The separations of photoproducts from the reaction of *p*-benzoquinone (7a) with diphenyl-*N*-

The indolin-2-one (14b) ( $R_F$  0.3) was a colourless solid; m.p. 254–256 °C;  $\nu_{\text{max}}$  3 300, 1 690, 1 500, and 1 465  $\text{cm}^{-1}$ ;  $\delta$  2.35 (3 H, s), 6.7–6.9 (3 H, m), and 7.25 (14 H, s) (Found: C, 82.4; H, 5.8; N, 3.9. C<sub>27</sub>H<sub>21</sub>NO<sub>2</sub> requires C, 82.9; H, 5.4; N, 3.6%).

From the reaction of (7a) with (15c), colourless needles ( $R_F$  0.3) were obtained; m.p. 238–241 °C;  $\nu_{\text{max}}$  3 250 and 1 690  $\text{cm}^{-1}$ .

*Preparation of Authentic Samples of the Spiro-β-lactams* (11a) and (17a).—3,3-Diphenyl- (11a) and 3,3-dimethyl-1-phenyl-1-azaspiro[3.5]nona-5,8-diene-2,7-dione (17a) were prepared as follows. To a benzene solution of (4-phenyl-imino)cyclohexa-2,5-dienone<sup>19</sup> cooled in ice-water was added dropwise a solution of diphenylketen<sup>20</sup> or dimethylketen<sup>21</sup> in benzene. The reaction mixtures were set aside

for 1 h at this temperature and the solvent was then removed *in vacuo*. The cycloaddition compounds (11a) and (17a) were then crystallised from ice-cold ether, filtered off, and then recrystallised from dichloromethane–light petroleum, yielding colourless crystals. The i.r. and n.m.r. spectra and m.p.s of these compounds were identical with the corresponding photoproducts (11a) and (17a) isolated from (9a) or the reaction of (7a) with (15a), respectively.

**Lewis-acid-catalysed Rearrangement of (9d).**—To a solution of the isolated spiro-2-imino-oxetan (9d) (391 mg, 1 mmol) in benzene (10 ml) was added 3 drops of boron trifluoride–ether (1:1), and the resulting mixture was stirred for 30 min at room temperature. After evaporation of the solvent, the partially oily residue was chromatographed over 10 g of silica gel (Wakogel C-200) with chloroform to afford 350 mg of 3,3-diphenyl-2,3-dihydro-5-hydroxy-*N*-(*p*-tolyl)-benzofuran-2-imine (13b); m.p. 253–256 °C (from chloroform–*n*-hexane) which was identical in spectral properties with the photoproduct isolated by t.l.c. ( $R_F$  0.5) from the reaction of (7a) and (8a) already described.

**Lewis-acid-catalysed Rearrangements of (11a) and (17a).**—Lewis-acid-catalysed rearrangements of the spiro- $\beta$ -lactams (11a) and (17a) were carried out similarly to that of (9d). 3,3-Diphenyl-5-hydroxy-1-phenylindolin-2-one (14a) was obtained from (11a), in a manner analogous to cyclohexadienone–phenol molecular migrations;<sup>11</sup> colourless solid (quantitative yield), m.p. 243–244 °C (from chloroform–*n*-hexane);  $\nu_{\max}$  3 240 and 1 685  $\text{cm}^{-1}$ ;  $\delta$  6.83 (3 H, m), 7.41 (10 H, s), 7.56 (5 H, s), and 7.71 (1 H, s). 3,3-Dimethyl-5-hydroxy-1-phenylindolin-2-one (18a) was also obtained from (17a); colourless needles, m.p. 212–214 °C (from chloroform–*n*-hexane);  $\nu_{\max}$  3 250 and 1 685  $\text{cm}^{-1}$ ;  $\delta$  1.42 (6 H, s), 6.68 (2 H, d), 6.7–6.8 (1 H, m), and 7.45 (5 H, s). The spectral properties of these compounds were similar to those of the photoproducts (14) and (18) obtained by t.l.c. separation from the reaction mixtures and also with those of the products (6) isolated by Ishibe and Yamaguchi.<sup>6</sup>

**Irradiation of the Spiro-2-imino-oxetan (9a).**—A nitrogen-purged ampoule containing a benzene solution of (9a) (500 mg; 1.3 mmol) was irradiated at room temperature for 24 h. The benzene was removed *in vacuo*, the products were crystallised from ether at –78 °C, and then recrystallised from ether to give (11a) as colourless crystals (22 mg); m.p. 124–126 °C;  $\nu_{\max}$  1 750 and 1 670  $\text{cm}^{-1}$ ;  $\delta$  6.50 (2 H, d,  $J$  10 Hz), 6.81 (2 H, d,  $J$  10 Hz), and 7.2–7.8 (10 H, m). A small amount of light petroleum was added to the ether filtrate and the resulting solution was chilled to give an

orange solid (45 mg), m.p. 165–167 °C (lit.,<sup>3</sup> 167–169 °C) (from benzene–light petroleum);  $\nu_{\max}$  3 025, 1 620, and 1 510  $\text{cm}^{-1}$ ;  $\delta$  6.35 (2 H, d,  $J$  10 Hz), 7.0–7.5 (12 H, m); identified as *p*-quinone diphenylmethide (12) on the basis of its m.p. and spectral data.

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