

## Photochemistry of Epoxyquinones. Part 7.<sup>1</sup> Photo-induced Cycloaddition of 2,3-Dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone to Olefins

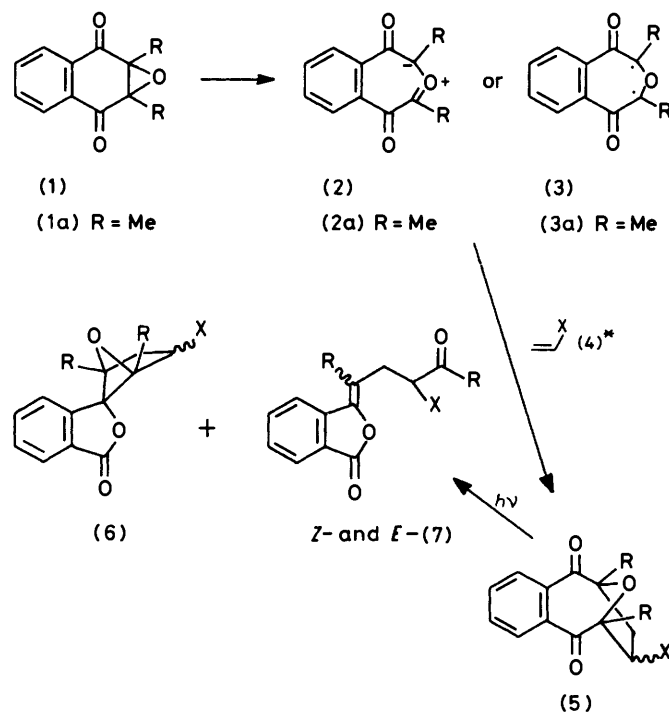
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Irradiation of 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (1a) in benzene gave the carbonyl ylide (2a) or the 1,3-diradical (3a), which was trapped with a variety of olefins, including simple alkenes, cycloalkenes, aromatic olefins, allyl alcohols, electron-rich olefins, and electron-deficient olefins. The excited state of (1a) was quenched by electron-rich olefins presumably *via* charge-transfer, while (2a) or (3a) react most readily with electron-deficient olefins. Cycloaddition of (2a) or (3a) to *cis*- and *trans*-but-2-ene proceeded stereospecifically. Further irradiation of the primary adducts gave the spirophthalide (5) and the alkylidene-phthalides *Z*-(7) and *E*-(7) *via* preferential  $\alpha$ -cleavage at the more crowded side. On the basis of the evidence of quantum yields and triplet lifetimes, this preference is believed to arise from the different efficiencies of the radical recombination of possible biradicals.

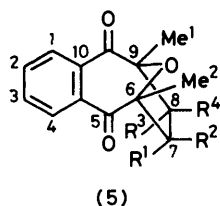
RECENTLY, we reported the photochemical production of the carbonyl ylide (2) or the 1,3-diradical (3) from several epoxy-naphthoquinones (1).<sup>2</sup> These products were trapped by olefins to give the tricyclic diketones (5), which underwent secondary photorearrangement and resulted in the formation of the spirophthalide (6) and the alkylidene-phthalides *Z*-(7) and *E*-(7) (Scheme 1). However, several questions remained unanswered in connection with the photoinduced cycloaddition of an epoxy-naphthoquinone to an olefin. First, the nature and lifetime of the excited state of (1) responsible for the production of (2) or (3) was unknown. Second, the relative reactivity and the stereochemistry of addition of

a variety of olefins toward (2) or (3) had not been well established, since the olefins hitherto examined had been limited to certain compounds such as 2-norbornene, dimethyl fumarate, and *N*-phenylmaleimide. Finally, studies on the mechanism of the secondary photorearrangement of (5) had been limited. Thus, we have examined the photochemical reactions of 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (1a) with a variety of olefins including simple alkenes, cycloalkenes, aromatic olefins, allyl alcohols, electron-deficient olefins, and electron-rich olefins. Here, we describe the effects of substituents of olefins on the nature and efficiency of the photoaddition process as well as the selective  $\alpha$ -



SCHEME 1 \* The olefins (4) used in the work are listed in Table 1.

cleavage at a more crowded site in the primary adducts (5).

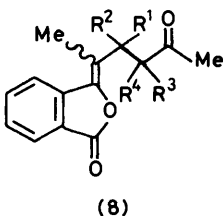
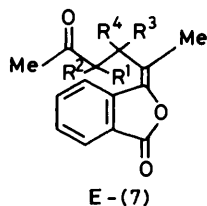
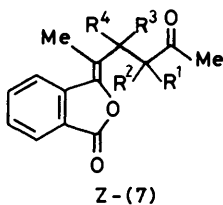
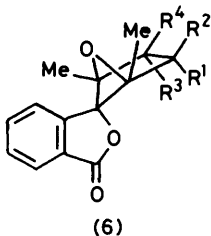
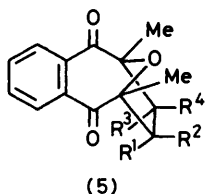


## RESULTS AND DISCUSSION

**Product Analysis.**—*Simple alkenes.* Irradiation of a benzene solution of compounds (1a) (0.015 M) containing 2-methylpropene (4a) (ca. 0.2 M, 5 °C, Pyrex) for up to 100% conversion followed by chromatographic separation over silica gel afforded the spirothalide (6a) (41%) and a 1 : 1 mixture of the alkylidenephthalides *Z*- and *E*-(7a) (26%). When the irradiation was stopped at 65%

conversion, the primary adduct (5a) was obtained in a yield of 42% along with (6a) (23%) and *E*- and *Z*-(7a) (14%). A brief exposure of (5a) under the irradiation conditions gave (6a) and *Z*- and *E*-(7a). Structure assignments to these photoproducts were made on the basis of their characteristic spectral data (see Table 5—10). Further, reduction of the mixture of *Z*-(7a) and *E*-(7a) with NaBH<sub>4</sub>, which gave *Z*-(9a) and *E*-(9a) in 40 and 36% yield, respectively, provided strong support for the structure of (7a).

In order to study the stereochemistry of the addition process, we examined the photoproducts with *trans*-but-2-ene (4b) and *cis*-but-2-ene (4c). Irradiation of (1a) and (4b) in benzene furnished a single primary adduct (5b) (92%) at 52% conversion of (1a). The <sup>1</sup>H n.m.r. spectrum of (5b) indicated the presence of two methyl singlets at δ 1.55 and 1.63, two methyl doublets at δ 1.10 (*J* 7 Hz) and 1.20 (*J* 7 Hz), and multiplets due to methine protons at δ 1.7—1.9, consistent with the



- a; R<sup>1</sup> = R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H  
 b; R<sup>1</sup> = R<sup>4</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H  
*c-en*; R<sup>1</sup> = R<sup>3</sup> = Me, R<sup>2</sup> = R<sup>4</sup> = H  
*c-ex*; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = R<sup>4</sup> = Me  
*d-en*; R<sup>1</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>3</sub>, R<sup>2</sup> = R<sup>4</sup> = H  
*d-ex*; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = R<sup>4</sup> = (CH<sub>2</sub>)<sub>3</sub>  
*e-en*; R<sup>1</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>4</sub>, R<sup>2</sup> = R<sup>4</sup> = H  
*e-ex*; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = R<sup>4</sup> = (CH<sub>2</sub>)<sub>4</sub>  
*f-en*; R<sup>1</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>5</sub>, R<sup>2</sup> = R<sup>4</sup> = H  
*f-ex*; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = R<sup>4</sup> = (CH<sub>2</sub>)<sub>5</sub>  
*g-en*; R<sup>1</sup> = R<sup>3</sup> = (CH<sub>2</sub>)<sub>6</sub>, R<sup>2</sup> = R<sup>4</sup> = H  
*g-ex*; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = R<sup>4</sup> = (CH<sub>2</sub>)<sub>6</sub>  
*h-en*; R<sup>1</sup> = Me, R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = H  
*i-en*; R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
*i-ex*; R<sup>1</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>2</sup> = Ph  
 j; R<sup>1</sup> = R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = H  
*l-ex*; R<sup>1</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>2</sup> = CH<sub>2</sub>OH  
*l'-en*; R<sup>1</sup> = CH<sub>2</sub>OAc, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
*m-ex*; R<sup>1</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>2</sup> = C(CH<sub>2</sub>)<sub>2</sub>OH  
*n-ex*; R<sup>1</sup> = Me, R<sup>2</sup> = CH<sub>2</sub>OH, R<sup>3</sup> = R<sup>4</sup> = H  
*o-ex*; R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = CH<sub>2</sub>OH  
*q-en*; R<sup>1</sup> = CO<sub>2</sub>Me, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup>  
*q-ex*; R<sup>1</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>2</sup> = CO<sub>2</sub>Me  
*q'-en*; R<sup>1</sup> = CO<sub>2</sub>H, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
*r-en*; R<sup>1</sup> = CO<sub>2</sub>Me, R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H  
*r-ex*; R<sup>1</sup> = Me, R<sup>2</sup> = CO<sub>2</sub>Me, R<sup>3</sup> = R<sup>4</sup> = H  
*r'-en*; R<sup>1</sup> = CO<sub>2</sub>H, R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H  
*s-en*; R<sup>1</sup> = CN, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
*s-ex*; R<sup>1</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>2</sup> = CN  
*t-en*; R<sup>1</sup> = CN, R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H  
*t-ex*; R<sup>1</sup> = Me, R<sup>2</sup> = CN, R<sup>3</sup> = R<sup>4</sup> = H  
*u-en*; R<sup>1</sup> = OEt, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
*u-ex*; R<sup>1</sup> = R<sup>3</sup> = R<sup>4</sup> = H, R<sup>2</sup> = OEt  
*v-en*; R<sup>1</sup> = OEt, R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H  
*v-ex*; R<sup>1</sup> = Me, R<sup>2</sup> = OEt, R<sup>3</sup> = R<sup>4</sup> = H  
 w; R<sup>1</sup> = R<sup>2</sup> = OEt, R<sup>3</sup> = R<sup>4</sup> = H  
 x; R<sup>1</sup>R<sup>2</sup> = SCH=CH, R<sup>3</sup> = R<sup>4</sup> = H

assigned *trans*-structure. On the other hand, irradiation of a benzene solution of (1a) in the presence of (4c) gave rise to a 5.8 : 1 mixture of the primary adducts (5c-*en*) and (5c-*ex*), which was separated by column chromatography on silica gel. In contrast to (5b), both (5c-*en*) and (5c-*ex*) had a symmetric *cis*-structure, which was evident from their simple <sup>1</sup>H n.m.r. spectra. The stereochemistry of (5c-*en*) and (5c-*ex*) was determined on the basis of their spectral data and comparisons to those obtained

duct (5d-*en*) (50%), the spirophthalide (6d) (2%), and the alkylidene phthalides *Z*-(7d) (15%) and *E*-(7d) (15%). G.c. analysis at a low conversion indicated the formation of another primary adduct (5d-*ex*) and the ratio of (5d-*en*) to (5d-*ex*) based on the peak intensity was 0.13, but (5d-*ex*) was neither isolated nor characterised. The stereochemistry of the primary adduct is difficult to determine with certainty, because only one of the isomers could be isolated. But *endo*-stereochemistry was tenta-

TABLE 1  
Photoinduced cycloaddition of epoxynaphthoquinone (1a) to olefins <sup>a</sup>

Run	Olefin	Conc. <sup>b</sup> (M)	Irrad. time (h)	Conversion (%)	Isolated yields (%) <sup>c</sup>				
					(5)		(6)	(7)	
					<i>endo</i>	<i>exo</i>		<i>Z</i>	<i>E</i>
1	CH <sub>2</sub> =CMe <sub>2</sub> (4a)	0.2	2	100	—	—	41	13	13
2	CH <sub>2</sub> =CMe <sub>2</sub> (4a)	0.2	0.25	65	42	—	23	7	7
3	MeCH=CHMe (4b)	0.2	0.25	52	92	—	—	—	—
4	MeCH=CHMe (4c)	0.2	0.25	59	81	14	—	—	—
5	CH=CH(CH <sub>2</sub> ) <sub>2</sub> ·CH <sub>3</sub> (4d)	0.11	2	90	50	—	2	15	15
6	CH=CH(CH <sub>2</sub> ) <sub>3</sub> ·CH <sub>3</sub> (4e)	0.06	2	98	35	—	<i>d</i>	29	26
7	CH=CH(CH <sub>2</sub> ) <sub>4</sub> ·CH <sub>3</sub> (4f)	0.08	2	92	49	—	<i>d</i>	21	21
8	CH=CH(CH <sub>2</sub> ) <sub>6</sub> ·CH <sub>3</sub> (4g)	0.06	2	97	—	41 <sup>e</sup>	<i>d</i>	—	29 <sup>f</sup>
9	Ph(Me)C=CH <sub>2</sub> (4h)	0.2	5	0	—	—	—	—	—
10	Ph(Me)C=CH <sub>2</sub> (4h)	0.03	2	65	—	5	46	12	31
11	PhCH=CH <sub>2</sub> (4i)	0.2	5	0	—	—	—	—	—
12	PhCH=CH <sub>2</sub> (4i)	0.05	4	69	16	19	15	23	23
13	Ph <sub>2</sub> C=CH <sub>2</sub> (4j)	0.02	5	82	—	—	40	12	13
14	Ph <sub>2</sub> C=CPh <sub>2</sub> (4k)	0.01	2	0	—	—	—	—	—
15	CH <sub>2</sub> =CH·CH <sub>2</sub> ·OH (4l)	0.1	0.5	82	84 <sup>g</sup>	—	—	6	5
16	CH <sub>2</sub> =CH·C(Me) <sub>2</sub> ·OH (4m)	0.1	0.5	78	62 <sup>g</sup>	—	—	—	—
17	CH <sub>2</sub> =C(Me)·CH <sub>2</sub> ·OH (4n)	0.125	0.5	60	47 <sup>g</sup>	—	—	23	18
18	MeCH=CH·CH <sub>2</sub> ·OH (4o)	0.1	0.5	75	60 <sup>g</sup>	—	—	12	4
19	HO·CH <sub>2</sub> ·CH=CH·CH <sub>2</sub> ·OH (4p)	0.1	1	84	84 <sup>g</sup>	—	—	—	—
20	CH <sub>2</sub> =CH·CO <sub>2</sub> Me (4q)	0.15	0.5	87	17	44	17	12	8
21	CH <sub>2</sub> =C(Me)·CO <sub>2</sub> Me (4r)	0.125	0.5	60	8.6	35	21	18	14
22	CH <sub>2</sub> =CHCN (4s)	0.2	0.5	72	86	—	4	2	2
23	CH <sub>2</sub> =C(Me)CN (4t)	0.15	0.5	77	66	—	8	7	12
24	EtO·CH=CH <sub>2</sub> (4u)	0.07	0.5	53	34	32	<i>h</i>	<i>h</i>	<i>h</i>
25	EtO(Me)C=CH <sub>2</sub> (4v)	0.06	1	77	9.4	14	—	22	20
26	(EtO) <sub>2</sub> C=CH <sub>2</sub> (4w)	0.05	1	60	—	—	<i>h</i>	<i>h</i>	<i>h</i>
27	S·CH=CH·C=CH (4x)	0.2	2	89	—	—	<i>h</i>	<i>h</i>	<i>h</i>

<sup>a</sup> Benzene solutions 0.015M in (1a) were used. <sup>b</sup> Concentrations of olefins. <sup>c</sup> Yields refer to the isolated ones based on the consumed amounts of (1a). <sup>d</sup> Trace amounts. <sup>e</sup> 1 : 1 Mixture of (5g-*en*) and (5g-*ex*). <sup>f</sup> 1 : 1 Mixture of *Z*-(7g) and *E*-(7g). <sup>g</sup> Isolated as the tetracyclic compounds (11). <sup>h</sup> Not determined. <sup>i</sup> The stereochemistry was not established.

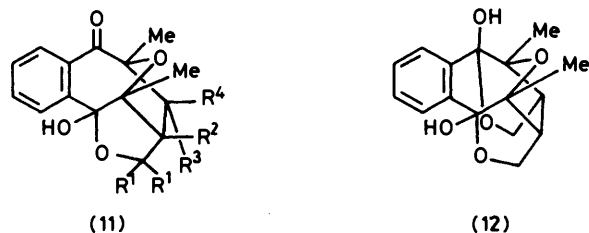
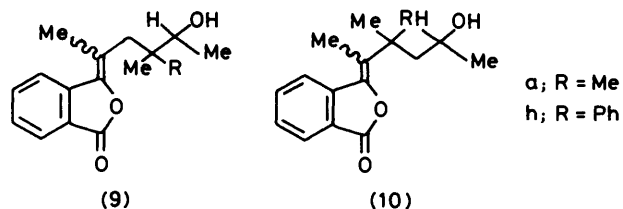
for related compounds in the series. The chemical shift observed for the methine protons at C-7 and C-8 in (5c-*ex*) was lower (at  $\delta$  2.55) relative to those (at  $\delta$  2.40) in (5c-*en*) owing to the proximity of the carbonyl groups to the methine protons. The doublet methyl protons at C-7 and C-8 in (5c-*en*) appeared at higher field (at  $\delta$  0.90) due to the shielding effects of the benzene ring, compared with those in (5c-*ex*) appearing at  $\delta$  1.13. The results with (4b) and (4c) revealed the stereospecific nature of the addition process, indicating that the cycloaddition of (2a) or (3a) to olefins is a concerted  $\pi_4 + \pi_2$  process.

**Cycloalkenes.** A benzene solution of (1a) (0.015 M) containing cyclopentene (4d) was irradiated at room temperature. Isolated products were the primary ad-

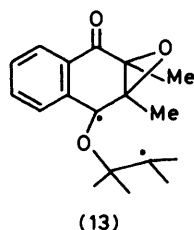
tively assigned for the major one on the basis of the comparison of the chemical shifts of methyl protons (at  $\delta$  1.62) with those of (5c-*en*) at  $\delta$  1.57 and of (5c-*ex*) at  $\delta$  1.42 and of the fact that the *endo*-adduct was preferentially formed in the reaction with (4c). Similar photoproducts were obtained in the reaction with cyclohexene (4e), cycloheptene (4f), and cyclo-octene (4g) (Table 1). Spirophthalides (6) and alkylidenephthalides (7) were again secondary photoproducts derived from primary adducts. But with cycloalkenes the spirophthalides (6d—g) were formed in very small amounts, compared with acyclic olefins.

**Aromatic olefins.** When irradiated in benzene solutions in the presence of 0.2M or more of 2-phenylpropene (4h) or styrene (4i) for a prolonged time, (1a) was re-

covered nearly quantitatively. This fact indicates that the photochemical ring opening of the oxiran ring to (2a) or (3a) from (1a) occurs *via* triplet excited state and is quenched by aromatic olefins with triplet energies much lower than that of (1a). But irradiation of a benzene solution of (1a) containing 0.03 M of 2-phenylpropene resulted in the formation of the primary adduct (5h-*ex*) (5%), the spirophthalide (6h) (46%), and the alkylidene phthalides *Z*-(7h) (12%) and *E*-(7h) (31%). The stereochemistry of (5h-*ex*) was readily determined on the basis of the highfield shift of the methyl protons at C-7 (at  $\delta$  1.03) due to the shielding effects of the phenyl group. None of the isomeric primary adduct (5h-*en*) was detected by g.c. nor  $^1\text{H}$  n.m.r. analysis even at a low conversion. The structure of the alkylidene phthalides came from the transformation of *E*-(7h) into the corresponding alcohol *E*-(9h) with  $\text{NaBH}_4$ . The  $^1\text{H}$  n.m.r. spectrum of *E*-(9h) showed the peaks at  $\delta$  1.18 (d,  $J$  7 Hz, 3 H), 1.34 (s, 3 H), 1.58 (s, 3 H), 3.02 and 3.34 (ABq,  $J$  15 Hz, 2 H), and 4.04 (q,  $J$  7 Hz, 1 H), only consistent with the structure of (9h) not with (10h). Similar irradiation



z;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$   
 m;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$   
 n;  $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{H}$ ,  $\text{R}^2 = \text{Me}$   
 o;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ,  $\text{R}^4 = \text{Me}$   
 p;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ,  $\text{R}^4 = \text{CH}_2\text{OH}$



of a benzene solution 0.015 M in (1a) and 0.05 M in styrene (4i) gave the primary adducts (5i-*en*) (16%) and (5i-*ex*) (19%), the spirophthalide (6i) (15%), and the alkylidene phthalides *Z*-(7i) (23%) and *E*-(7i) (23%). The highfield shift of the methyl protons at C-6 (at  $\delta$  1.13) in (5i-*ex*) characterised the *exo*-stereochemistry of the phenyl group in (5i-*ex*). Three products, the spirophthalide (6j) (40%), and the alkylidenephthalides *Z*-(7j) (12%) and *E*-(7j) (13%), were formed by irradiating a benzene solution of (1a) containing 0.02 M of 1,1-diphenylethylene (4j). Attempts to isolate the primary adduct (5j) were unsuccessful, since the rate of secondary photorearrangement of (5j) is so rapid that (5j) was merely detected in small amounts by a g.c. technique. Irradiation of a benzene solution of (1a) and tetraphenylethylene (4k) (0.01 M) resulted in the complete recovery of the starting materials.

*Allyl alcohols.* As noted above, primary adducts (5) are generally photolabile and readily converted into secondary photoproducts. Thus, isolation of compound (5) usually requires work-up at a relatively low conversion of (1a). In sharp contrast, we have found that the *endo*-primary adduct derived from the reaction with allyl alcohol is strikingly photostable owing to its hemiacetal structure which masks the photosensitive diketone form.<sup>3</sup> Typically, irradiation of a benzene solution of (1a) (0.015 M) and allyl alcohol (4l) (0.1 M) followed by column chromatography on silica gel gave the tetracyclic adduct (11l) in a high yield, 84%, along with the alkylidenephthalides *Z*-(7l) (6%) and *E*-(7l) (4%). The  $^{13}\text{C}$  n.m.r. spectrum of (11l) revealed the presence of one ketone carbon at  $\delta$  203.2 and hemiacetal carbon at  $\delta$  107.4 p.p.m. Acetylation of (11l) with perchloric acid in acetic anhydride gave a 78% yield of the diketone-acetate (5l'-*en*). However, g.c. analysis indicated the presence of another primary adduct at an early stage of the reaction. The major peak was found to correspond to (11l). Thus, the minor one seemed to correspond to the isomeric *exo*-primary adduct (5l'-*ex*), which could not be isolated. The peak ratio of (11l) to the minor one was 4.5 at 5% conversion of (1a) but decreased steadily as the reaction proceeded. Since an extended exposure of (11l) under the same irradiation conditions merely brought about the formation of *Z*- and *E*-(7l) in very small amounts, *Z*- and *E*-(7l) appeared to be largely derived from the expected (5l'-*ex*). Several substituted allyl alcohols such as 2-methylbut-3-en-2-ol (4m), methallyl alcohol (4n), and *trans*-crotyl alcohol (4o) were similarly found to react with (2a) or (3a), giving the tetracyclic compounds (11) as the major products. In the hope of obtaining a cage compound (12), the photochemical reaction of (1a) with *cis*-but-2-ene-1,4-diol (4p) was attempted, but only monohemiacetal (11p) was formed in 84% yield. The result with allyl alcohols may imply the possibility that photo-labile cycloadducts can be obtained even in the photo-induced cycloaddition by immediately masking the photo-sensitive group after the cycloaddition takes place.

*Electron-deficient olefins.* In order to investigate the effects of substituents of olefins on the nature and efficiency of the photoaddition process, we explored the photochemical reaction of (1a) with both electron-deficient and electron-rich olefins. Five products, the isomeric primary adducts (5q-*en*) (17%) and (5q-*ex*) (44%), the spirophthalide (6q) (17%), and the alkylidenephthalides *Z*-(7q) (12%) and *E*-(7q) (8%), were obtained with methyl acrylate (4q). The

stereochemistry of the methoxycarbonyl group in (5q) was deduced by the chemical shift of the methine protons and the methoxy-protons. The methine proton of (5q-*ex*) appeared at lower field ( $\delta$  3.38) due to the deshielding effects of the carbonyl group, compared with that of (5q-*en*) at  $\delta$  3.20. On the other hand, the methoxy-protons of (5q-*en*) appeared at higher field ( $\delta$  3.67) due to the shielding effect of the benzene ring, compared with that of (5q-*ex*) at  $\delta$  3.80. These structural assignments were unambiguously established by the independent synthesis of (5q-*en*) from (11l). Jones' oxidation of (11l) afforded the acid (5q'-*en*), which was treated with diazomethane in ether to give (5q-*en*) in 75% overall yield. The position of the methoxycarbonyl group in the alkylidene-phthalides (7q) was determined on the basis of the fact both *Z*- and *E*-(7q) were readily deprotonated by  $K_2CO_3$  in  $CDCl_3$  and were alkylated with methyl iodide in dimethylformamide (DMF), giving the alkylidene-phthalides *Z*-(7r) and *E*-(7r) in 79 and 86% yields, respectively, which were in all respects identical with the secondary photoproducts derived from the reaction with methyl methacrylate (4r). Irradiation of a benzene solution of (1a) in the presence of methyl methacrylate (4r) led to the formation of the primary adducts (5r-*en*) (8.6%) and (5r-*ex*) (35%), the spirophthalide (6r) (21%), and the alkylidene-phthalides *Z*-(7r) (18%) and *E*-(7r) (14%). The *endo*-primary adduct (5r-*en*) was independently synthesized from (11m) in 56% overall yield.

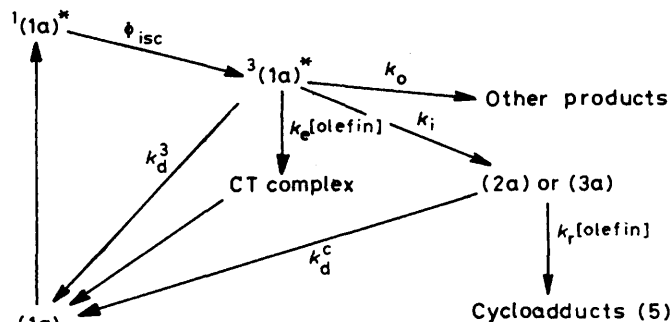
Irradiation of (1a) with either acrylonitrile (4s) or methacrylonitrile (4t) resulted in the predominant formation of the *endo* primary adduct (5s-*en*) (86%) or (5t-*en*) (66%), along with the secondary photoproducts, (6s) (4%), *Z*-(7s) (2%), and *E*-(7s) (2%), or (6t) (8%), *Z*-(7t) (7%), and *E*-(7t) (12%). The *endo*-stereochemistry of the cyano-group in (5s-*en*) and (5t-*en*) was confirmed by the transformation, through alkaline hydrolysis and subsequent methylation with diazomethane, into (5q-*en*) and (5r-*en*) in overall yields of 55 and 63%, respectively. The alkylidene-phthalides *Z*-(7s) and *E*-(7s) were easily deprotonated with  $K_2CO_3$  and were alkylated with methyl iodide in DMF to give *Z*-(7t) and *E*-(7t) in yields of 72 and 75%, respectively. These transformations provided strong evidence for the assigned structures of both *Z*- and *E*-(7s) and *Z*- and *E*-(7t).

**Electron-rich olefins.** Finally, the carbonyl ylide (2a) or 1,3-diradical (3a) was trapped with electron-rich olefins such as ethyl vinyl ether (4u), 2-ethoxypropene (4v), and 1,1-diethoxyethylene (4w). In the photochemical reaction with (4u), we obtained the primary adducts (5u-*en*) (34%) and (5u-*ex*) (32%).<sup>4</sup> The stereochemical assignment of the ethoxy-group rested on the significant difference of the chemical shifts of the ethoxy-protons. The methyl protons of the ethoxy-group in (5u-*en*) appeared at higher field ( $\delta$  0.74) owing to the shielding effects of the benzene ring, compared with those of (5u-*ex*) appearing at  $\delta$  1.23. Photochemical reaction of (1a) with (4v) gave similarly the primary adducts (5v-*en*) (9.4%) and (5v-*ex*) (13.8%), and the alkylidene-

phthalides *Z*-(7v) (22%) and *E*-(7v) (20%). The primary adduct (5w) was isolated in the reaction with (4w). Interestingly, thiophen (4x) was found to be able to react with (2a) or (3a) resulting in the formation of the primary adduct (5x) in a yield of 7%, although the major course of the reaction was rather polymeric.

**Reaction Mechanism.**—The photoinduced cycloaddition of (1a) to olefins consists primarily of two processes, namely photochemical oxiran ring opening leading to the formation of (2a) or (3a) and 1,3-dipolar cycloaddition of olefin to (2a) or (3a). The photoreaction of (1a) was quenched by naphthalene ( $E_t = 61$  kcal/mol) or piperylene ( $E_t = 58$  kcal/mol) but insufficiently by biphenyl ( $E_t = 66$  kcal/mol), and was sensitised by xanthone ( $E_t = 74$  kcal/mol), indicating the triplet reaction.

Quantum yields for the formation of the primary adducts (5) in benzene solution 0.015 M in (1a) containing various concentrations of olefin were determined at 313 nm by using valerophenone as the chemical actinometer.<sup>5</sup> At [olefin] > 0.01M, the quantum yields decrease with increasing concentration of olefin, significantly in the case of electron-rich olefins or aromatic olefins. The total quantum yield ( $\Phi_t$ ) can be expressed as the product of two separate probabilities as shown in equation (1), where  $\Phi_o$  is the probability that (2a) or (3a) will be produced after photoexcitation and  $\Phi_p$  is the probability that (2a) or (3a) will react with olefin to give the primary adducts. Since  $\Phi_p$  must be larger at higher olefin concentrations, the decrease in  $\Phi_t$  should be attributed to the decrease in  $\Phi_o$ . Assuming that olefin



SCHEME 2

quenches the triplet excited state of (1a) as shown in Scheme 2,  $\Phi_t$  is expressed in equation (2).

$$\Phi_t = \Phi_o \cdot \Phi_p \quad (1)$$

$$\Phi_t = \Phi_{isc} \cdot \frac{k_i}{k_d^3 + k_i + k_o + k_e[olefin]} \cdot \frac{k_r[olefin]}{k_d^c + k_r[olefin]} \quad (2)$$

If  $k_r[olefin] \gg k_d^c$ ,

$$\Phi_t = \Phi_{isc} \cdot \frac{k_i}{k_d^3 + k_i + k_o + k_e[olefin]} \quad (3)$$

$$\Phi_t^{-1} = K^{-1} \cdot (1 + k\tau^0[olefin]) \quad (4)$$

where

$$K = \Phi_{isc} \cdot \frac{k_i}{k_d^3 + k_i + k_o}, \tau^0 = \frac{1}{k_d^3 + k_i + k_o} \quad (5)$$

Plots of reciprocal quantum yields *vs.* olefin concentrations were found to be linear at [olefin] > 0.1 M with virtually the same intercept (1.75) but with different slopes (see Figure), consistent with the reaction scheme

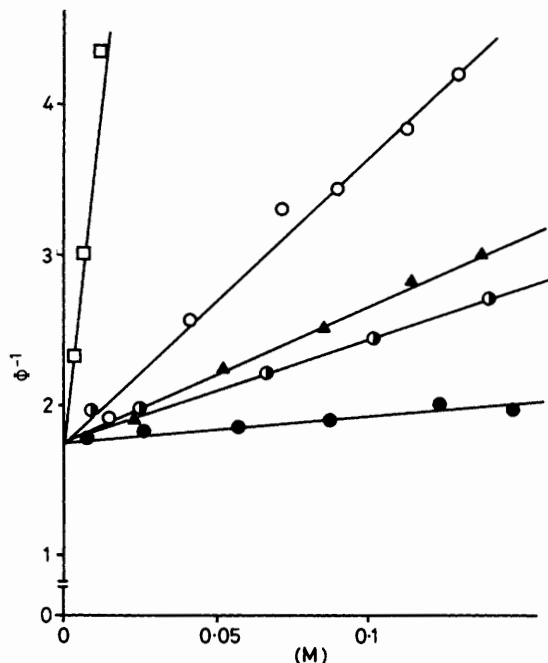


FIGURE Plots of reciprocal quantum yields for the formation of the primary adducts (5) *vs.* olefin concentrations; (4f) ●, (4i) □, (4q) ●, (4r) ▲, and (4u) ○

described in Scheme 2. From the intercept and slopes, values of  $K$  and  $k_e\tau^0$  were determined. The value of  $K$  (0.57) may be regarded as the inherent quantum yield for the formation of (2a) or (3a). In order to estimate the life time,  $\tau^0$ , of triplet (1a), benzene solutions 0.015 M in (1a) and 0.02 M in cyclohexene (4e) containing various concentrations of naphthalene were irradiated in parallel with the valerophenone actinometer.<sup>5</sup> Stern-Volmer plots were linear to  $\Phi^0/\Phi = 6$  with a slope ( $k_q\tau$ ) of 99

$M^{-1}$ . With  $k_q = 5 \times 10^9 M^{-1}s^{-1}$ ,<sup>6</sup>  $1/\tau = 5.1 \times 10^7 s^{-1}$ , where

$$\tau = \frac{1}{k_d^3 + k_i + k_o + k_e[0.02]} \quad (6)$$

From  $k_e\tau^0 = 3.2 M^{-1}$  and equation (6),  $k_e$  for cyclohexene and  $1/\tau^0$  were calculated to be  $1.5 \times 10^8 M^{-1}s^{-1}$  and  $4.7 \times 10^7 s^{-1}$ , respectively. Results with other olefins are listed in Table 2. The  $1/\tau^0$  value equals the sum of the rate constants for oxiran ring opening ( $k_i$ ) and other chemical reactions ( $k_o$ ) such as  $\alpha$ -cleavage<sup>7</sup> and non-radiative decay ( $k_d^3$ ). Values of  $k_d^3 \approx 3 \times 10^5 s^{-1}$  have been reported for a number of aryl ketones in benzene solution.<sup>8</sup> Such values are small compared to  $1/\tau^0$ , indicating that  $k_i \approx 1/\tau^0$ .

It seems that quenching by electron-rich olefins (4u) and (4v) involves charge-transfer. The increase in  $k_e$  upon going from (4u) to (4v) is probably the best evidence for this inference. Here electronic effects predominate over steric effects.<sup>9</sup> The same trend that methyl group on the double bond enhances  $k_e$  by a factor of 2–6 indicates charge-transfer quenching for simple alkenes and electron-deficient olefins as well as electron-rich olefins. Since oxetan-type products were not found under our experimental conditions, it is likely that the charge-transfer complex largely collapses to the starting materials but not to a 1,4-biradical such as (13). Kochevar and Wagner examined the quenching of the type II photoelimination of butyrophenone ( $E_t = 72$  kcal/mol) by a variety of olefins and concluded that charge-transfer predominates for electron-rich olefins, while energy-transfer for electron-deficient olefins such as chloroethylenes and fumaronitrile.<sup>10</sup> Although the triplet energy of (1a) is not determined accurately, it is deduced to be in the range of 65–70 kcal/mol on the basis of the quenching experiments. Thus, it seems unlikely that triplet (1a) was quenched by methyl methacrylate or methacrylonitrile *via* energy transfer. Quenching by styrene or 2-phenylpropene is nearly

TABLE 2  
Photoinduced cycloaddition of (1a) to olefins

Olefin	$\Phi_1^a$	$k_e\tau^0 (M^{-1})^b$	$10^{-8}k_e (M^{-1} s^{-1})^c$	<i>endo/exo</i> <sup>d</sup>	Relative <sup>e</sup> reactivity
(4d)	0.42	4.3	2.0	7.4	2.3
(4e)	0.35	3.2	1.5	13.0	0.078
(4f)	0.49	4.0	1.9	4.8	1.0
(4g)	0.44	4.4	2.1	2.35	7.4
(4h)	0.12	68	32	<i>exo</i> rich	1.02
(4i)	0.094	105	49	0.28	32
(4l)	0.51	1.3	0.61	4.5	1.4
(4n)	0.52	2.7	1.3	1.6	0.17
(4o)	0.46	4.4	2.1	3.5	0.052
(4q)	0.54	0.85	0.40	0.35	32
(4r)	0.46	5.0	2.4	0.25	4.2
(4s)	0.53	2.3	1.1	<i>endo</i> rich	8.2
(4t)	0.41	7.8	3.7	<i>endo</i> rich	0.74
(4u)	0.37	11	5.2	1.4	0.7
(4v)	0.22	28	13	1.1	0.02
(4y) <sup>f</sup>	0.54	1.1	0.52	2.3	1.0

<sup>a</sup> Quantum yields for the formation of the primary adducts (5) at [olefin] = 0.1M. <sup>b</sup> Least-squares slopes of linear Stern-Volmer plots in the Figure. <sup>c</sup> Calculated on the assumption that  $1/\tau^0 = 4.7 \times 10^7 s^{-1}$ . <sup>d</sup> The *endo/exo* ratio of the primary adducts. <sup>e</sup> Relative reactivity toward (2a) or (3a) with hex-1-ene as the standard. <sup>f</sup> Hex-1-ene.

diffusion-controlled and undoubtedly involves primarily, and perhaps exclusively, energy transfer.

While quenching experiments indicate that the oxiran ring opening is triplet in character and the nascent ylide or 1,3-diradical is formed in the triplet state,<sup>11</sup> the subsequent 1,3-dipolar cycloaddition reactions are stereospecific, which is evident from the results obtained upon addition of either *trans*- or *cis*-but-2-ene, *trans*-crotyl alcohol, or *cis*-but-2-ene-1,4-diol to (2a) or (3a). These are features which characterise the corresponding ground-state reactions and thus indicate that intersystem crossing to the singlet manifold occurs prior to the cycloaddition.<sup>12</sup> The *endo-exo* ratios of the primary adducts were determined by g.c. analysis at low conversions (e.g. <5%) and are included in Table 2. Generally, *endo-exo* stereoselectivity is poor. But there exists a tendency toward *endo*-orientation for electron-releasing substituents such as alkyl, hydroxymethyl, and ethoxy-groups, and towards *exo*-orientation for electron-attracting substituents such as methoxycarbonyl and phenyl

that of (5q-*en*) + (5q-*ex*). Thus it is clear that the quenching of triplet (1a) bears no relation to product formation. The relative reactivities thus obtained are listed in Table 2. In contrast to the rate constants for the quenching of triplet (1a), electron-deficient olefins are more reactive than electron-rich olefins. A methyl group on the double bond reduced the reactivity toward (2a) or (3a) by a factor of *ca.* 10. These effects of the methyl group are probably the result of both electronic and steric factors and seem to operate to a greater extent in a cycloaddition transition state in which the methyl group is oriented *exo*. From the order of the relative reactivities of olefins, it is indicated that the interaction between the highest-occupied molecular orbital (HOMO) of (2a) and the lowest-unoccupied molecular orbital (LUMO) of olefin is most important.<sup>13</sup> It is interesting to note that an aromatic olefin such as styrene (4i), which is an efficient triplet quencher, is very reactive toward (2a) or (3a). This result is consistent with the above conclusions, since LUMO energies of aromatic

TABLE 3  
Competitive experiment between (4u) and (4q)

Run	Olefins (Concn)		$\Phi_{\text{obs.}}^b$	$\Phi_{\text{calc.}}^c$	Products (%)		Relative reactivity of (4q) to (4u)
	(4u) (M)	(4q) (M)			(5u)	(5q)	
1	0.1	0.1	0.24	0.26	2.1	97.9	46.6
2	0.2	0.1	0.15	0.17	4.1	95.9	46.8
3	0.2	0.05	0.17	0.18	8.0	92.0	46

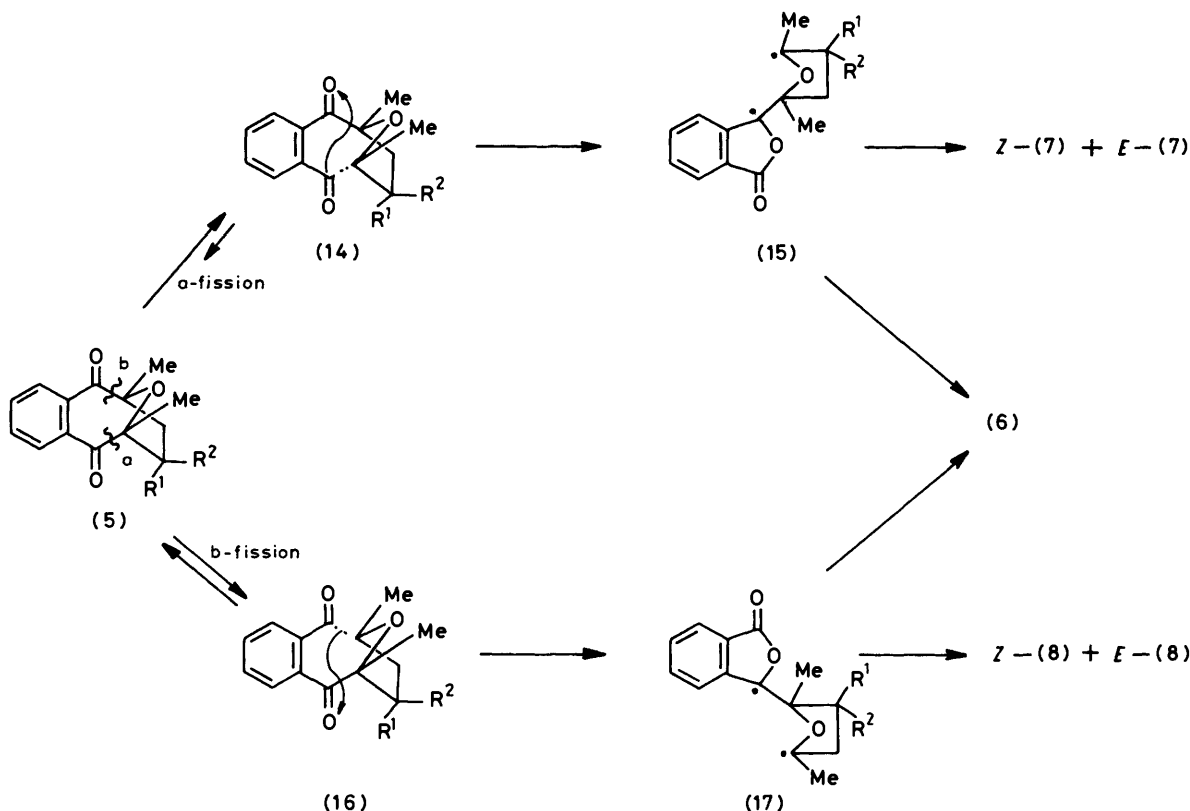
<sup>a</sup> Benzene solutions 0.015M in (1a) were used. <sup>b</sup> Quantum yield for the disappearance of (1a). <sup>c</sup> Calculated quantum yield for the disappearance of (1a) based on  $k_e\tau^0$  values in Table 2.

groups, with the exception of the cyano-group which showed a prominent *endo*-orientating tendency. These orientations may be accounted for by considering the dipole-dipole interactions rather than secondary orbital overlap or steric factors, but with acrylonitrile or methacrylonitrile some other interactions, presumably secondary  $\pi$ -orbital overlap, would predominate over the dipole-dipole interaction.

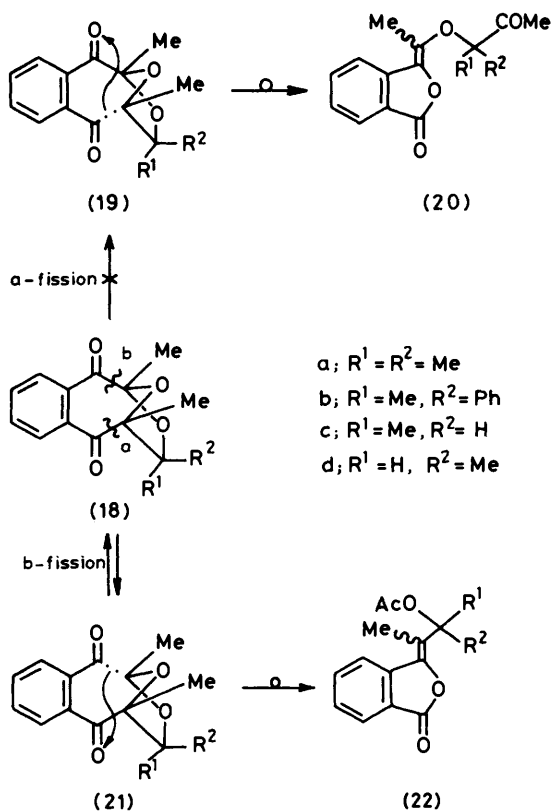
The relative reactivities of olefins toward (2a) or (3a) were determined by competition experiments. Typically, experiments for ethyl vinyl ether (4u) *vs.* methyl acrylate (4q) are described (Table 3). Benzene solutions 0.015 M in (1a) containing various concentrations of (4u) and (4q) were irradiated for a short enough time for the ratio of the olefins not to change significantly from the initial ratio. The ratio of (5u-*en*) + (5u-*ex*) to (5q-*en*) + (5q-*ex*) was divided by the concentration ratio of the olefins, giving the relative reactivity of (4u) to (4q). The relative reactivity is not affected by the concentration ratio. In Table 3 are included the observed quantum yields for the disappearance of (1a) and the calculated ones based on the  $k_e\tau^0$  values in Table 2, assuming that quenching by each olefin is simply additive. Good agreement of both values indicates the assumption is correct. Accordingly, in run 3 in Table 3, *ca.* 67% of the triplet (1a) is quenched by (4u), while only 2.6% by (4q). However, the amount of (5u-*en*) + (5u-*ex*) is merely 11.5% as much as

olefins should be lower. In the case of tetraphenylethylene (4k), steric hindrance would be too large for the addition to take place.

The primary adducts (5) undergo novel photorearrangement to give the spirophthalides (6) and the alkylidenephthalides (7) simultaneously. The photorearrangement is likely to begin with  $\alpha$ -cleavage leading to a biradical (14), followed by lactonisation to give a 1,4-biradical (15) which cyclizes to give (6) or isomerizes to give (7) (Scheme 3). However, as the initial step, another biradical (16) could be formed as well as (14) and collapse to the regioisomeric alkylidenephthalides *Z*- and *E*-(8) along with (6). Therefore, the predominant formation of (7) over (8) here requires the preference of a-fission over b-fission (designated in Scheme 3) as the reaction course. On the other hand, photolysis of (18a-d) led to the predominant formation of *Z*- and *E*-(22), which were derived from b-fission (designated in Scheme 4).<sup>13</sup> Predominant b-fission in (18) may be simply accounted for in view of the smaller bond energy of the b-bond which is weakened by two adjacent oxygen atoms, compared with that of the a-bond. But it appears to be difficult to rationalize the results for (5) on the basis of simple energetic considerations of the bond to be cleaved. In order to obtain more information on the mechanism of the reaction, we have studied the quantitative aspects of the secondary photorearrangement of (5). The photoreactions of (5) and (18) were



SCHEME 3



SCHEME 4

quenched by naphthalene or piperylene and were sensitized by xanthone, thus indicating the occurrence of triplet reaction. Quantum yields for the photorearrangement and triplet life times of (5) were determined at low conversions (*e.g.*, <4%) with the use of the valerophenone actinometer and the naphthalene quencher. The data are collected in Table 4. Results for compounds (18) are included for purposes of comparison.

TABLE 4

Quantum yields and kinetic data for the photorearrangement of (5) and (18)

Reactant	$\Phi^b$	$k_q\tau(\text{M}^{-1})^c$	$10^{-6} 1/\tau(\text{s}^{-1})^d$
(5a)	0.57	600	8.3
(5b)	0.21	510	9.8
(5c-en)	0.24	570	8.8
(5d-en)	0.43	550	9.1
(5f-en)	0.18	700	7.1
(5h-ex)	0.69	510	9.8
(5i-ex)	0.36	550	9.1
(5q-ex)	0.51	460	11.0
(5r-ex)	0.62	440	11.4
(5s-en)	0.47	780	6.4
(5t-en)	0.57	550	9.1
(18a)	0.010	90	56
(18b)	0.021	85	59
(18c)	0.0086	105	48
(18d)	0.0094	130	38

<sup>a</sup> Benzene solutions 0.015M in (5) or (18) were used. <sup>b</sup> Quantum yields for the disappearance of (5) or (18). <sup>c</sup> Least-squares slopes of linear Stern-Volmer plots in benzene solutions using naphthalene as the triplet quencher,  $\pm 10\%$ . <sup>d</sup> Assuming  $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .



It is very significant that all eleven primary adducts (5) examined have virtually the same triplet lifetimes within experimental error, even though they rearrange with varying efficiencies. Since all eleven diketones cleave to biradicals of comparable stability, it would be expected that they would do so at comparable rates. On the other hand, the triplet lifetimes of (18) are by a factor of 5–6 shorter than those of the corresponding (5). The decrease in lifetime  $\tau$  upon replacement of the C-7 methylene by oxygen is entirely consistent with the primary triplet photoprocess for (5) and (18) being one of  $\alpha$ -cleavage to yield a biradical, since (18) can cleave to give a more stabilized biradical (21).

However, the quantum yields seem to be determined primarily by the behaviour of the biradical intermediate. Substituents at C-7 in (5) enhance the quantum yield, while replacement of C-7 methylene with oxygen reduces the quantum yield drastically. It is well recognized that radical recombination is one of the most common reactions derived from radical pairs from  $\alpha$ -cleavage of alkyl aryl ketones.<sup>14</sup> Thus, the low quantum yields for (18) might reflect the efficient cage recombination of the biradical (21), while considerably higher quantum yields for (5) might reflect the decreased propensity of the intermediate biradical (14) to recouple. It is plausible in this rigid system that substituents at C-7 retard the radical recombination or render the biradical conformation favourable for the lactonisation going to products sterically through something like buttressing effects, while oxygen at C-7 will exert negligible steric effects for radical reactions. Therefore, we may conclude that the preference of a-fission over b-fission in (5) as the reaction course arises from the difference between the efficiencies of the recombination in the biradicals (14) and (16).

#### EXPERIMENTAL

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. I.r. spectra were recorded on a Hitachi Model 260–10. <sup>1</sup>H N.m.r. spectra were recorded on a JEOL PS-100 and a JEOL JMN-C-60HL machine and chemical shifts are reported in p.p.m. on the  $\delta$  scale from internal Me<sub>4</sub>Si. <sup>13</sup>C N.m.r. spectra were recorded on a JEOL FX-100. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. G.c. analyses were performed on a Hitachi Model 163, using a 3 $\phi$   $\times$  1 m stainless-steel column packed with 10% SE-30 on Celite 545 AW. Preparative separations were performed by column chromatography over silica gel (Wakogel C-200). U.v. irradiations were carried out in a Pyrex vessel (Eikosha EHB-WF) under an argon atmosphere with an Eikosha 300-W high pressure Hg lamp.

*General Procedure for the Photochemical Reaction of (1a) with Olefin.*—Solvent benzene was purified by distillation from benzophenone ketyl solution. The olefins (4a) (99%), (4b) (99%), (4c) (98%), (4f) (99%), (4m) (98%), (4o) (93%), (4p) (95%), (4q) (98%), (4r) (98%), (4s) (98%), (4u) (99%), and (4x) (99%) were purchased from Tokyo Kasei Kogyo Co. The following olefins were obtained from Nakarai Kagaku Co.: (4d) (99%), (4e) (99%), (4h) (99%), (4i) (98%), (4l) (99%), (4n) (99%), (4t) (97%), and (4y) (98%). The following olefins were obtained from Aldrich Chemical Co.:

(4j) (97%) and (4k) (98%). The olefin (4v) was prepared by the method of Dolliver<sup>16</sup> and (4w) was prepared by the method of McElvain and Kundiger.<sup>17</sup> The olefins were purified just prior to use by preparative g.c.

Argon was bubbled through a solution of (1a)<sup>2</sup> and olefin in benzene (400 ml) in a Pyrex vessel for 10 min and then irradiated with water cooling for an appropriate period of time. The progress of the reaction was followed. After removal of the solvent and excess of olefin, the residual yellow oil was chromatographed over silica gel column, using ether–hexane as the eluant. Final purification was usually accomplished by preparative t.l.c. and recrystallization. M.p.s, i.r. and <sup>1</sup>H n.m.r. spectral results and the elemental analyses of photoproducts are summarized in Table 5–12.

<sup>13</sup>C N.m.r. data of selected photoproducts are as follows:

(6h): 11.1 (q), 14.6 (q), 20.6 (q), 48.2 (t), 50.9 (s), 89.6 (s), 92.3 (s), 99.3 (s), 125.7 (d), 126.3 (d), 126.7 (s), 127.3 (d), 127.5 (d), 128.6 (d), 129.7 (d), 134.2 (d), 145.2 (s), 146.4 (s), and 168.7 (s) p.p.m.

Z-(7h): 18.2 (q), 20.2 (q), 25.6 (q), 42.1 (t), 56.3 (s), 120.2 (s), 123.1 (d), 125.2 (d), 126.4 (d), 126.8 (d), 127.2 (d), 128.5 (d), 134.1 (d), 138.2 (s), 141.9 (s), 143.3 (s), 166.4 (s), and 209.5 (s) p.p.m.

E-(7h): 18.9 (q), 19.3 (q), 25.6 (q), 39.9 (t), 56.2 (s), 121.7 (s), 123.0 (d), 125.5 (d), 126.6 (d), 127.5 (d), 128.6 (d), 129.0 (d), 134.2 (d), 138.2 (s), 142.2 (s), 143.7 (s), 166.5 (s), and 209.8 (s) p.p.m.

(5i-en): 23.9 (q), 24.4 (q), 41.3 (t), 55.2 (d), 89.1 (s), 92.5 (s), 124.7 (d), 126.9 (d), 127.5 (d), 128.5 (d), 129.1 (d), 129.7 (d), 130.2 (d), 134.3 (s), 135.2 (s), 135.8 (s), 203.5 (s), and 203.9 (s) p.p.m.

(5i-ex): 21.4 (q), 23.5 (q), 42.8 (t), 65.0 (d), 89.2 (s), 91.5 (s), 126.8 (d), 127.3 (d), 128.5 (d), 129.0 (d), 129.3 (d), 132.0 (d), 133.1 (d), 134.1 (s), 135.5 (s), 138.1 (s), 206.8 (s), and 209.2 (s) p.p.m.

(6j): 22.2 (q), 22.6 (q), 52.1 (t), 61.2 (s), 89.6 (s), 91.0 (s), 98.2 (s), 125.3 (d), 125.8 (d), 126.0 (d), 126.3 (d), 127.2 (d), 127.8 (d), 129.0 (d), 129.8 (d), 130.2 (s), 134.1 (d), 145.1 (s), 145.5 (s), 145.7 (s), and 167.7 (s) p.p.m.

(11l): 19.5 (q), 24.9 (q), 44.1 (t), 50.2 (d), 71.3 (t), 89.7 (s), 94.4 (s), 107.3 (s), 123.3 (d), 126.5 (d), 129.2 (d), 130.7 (d), 137.1 (s), 140.5 (s), and 206.3 (s) p.p.m.

*Reduction of Z- and E-(7a) with NaBH<sub>4</sub>.*—A 1 : 1 mixture of the alkylidene-phthalides Z- and E-(7a) (100 mg), dissolved in methanol (20 ml), was reduced with NaBH<sub>4</sub> (20 mg). The mixture was stirred for 1 h at room temperature, poured into water, and extracted twice with ether. Separation on a short silica gel column gave Z-(9a) (40 mg, 40%) and E-(9a) (36 mg, 36%).

(Z)- and (E)-3-(4-Oxo-1,3,3-trimethylpentylidene)phthalide (7a).— $\nu_{\max}$  (CCl<sub>4</sub>) 2 980, 1 770, 1 765, 1 690, 1 250, and 730 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.24 (s, 6 H), 1.27 (s, 6 H), 2.05 (C=C-Me), 2.14 (C=C-Me), 2.27 (s, 6 H, CO-Me), 2.81 (s, 2 H), 2.93 (s, 2 H), and 7.4–8.0 (m, 8 H).

(Z)-3-(4-Hydroxy-1,3,3-trimethylpentylidene)phthalide Z-(9a): m.p. 124–125 °C,  $\nu_{\max}$  (KBr) 3 480, 2 970, 1 770, 1 590, 1 250, and 730 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.05 (s, 6 H), 1.22 (d, J 6 Hz, 3 H), 2.20 (s, C=C-Me), 2.67 (s, 2H), 3.55 (q, J 6 Hz, CH-OH), and 7.4–7.7 (m, 4 H) (Found: C, 73.65; H, 8.0. C<sub>16</sub>H<sub>20</sub>O<sub>3</sub> requires C, 73.82; H, 7.74%).

(E)-3-(4-Hydroxy-1,3,3-trimethylpentylidene)phthalide E-(9a): m.p. 98–99 °C  $\nu_{\max}$  (KBr) 3 560, 2 990, 1 775, 1 600, 1 250, and 790 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 0.95 (s, 6 H), 1.47 (d, J 7 Hz, 3 H), 2.13 (s, C=C-Me), 2.85 (s, 2 H), 3.67 (q, J 7 Hz, CH-

TABLE 5

Physical properties of the primary adducts (5)

Compd. (5a)	M.p. (°C) 85—85	Formula C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	Found (%) C, 74.55 H, 7.05	Required (%) 74.39 7.02	$\nu_{\max.}/\text{cm}^{-1}$ (KBr) 2 990, 1 690, 1 305, 1 250, 730
(5b)	140—141	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	C, 74.35 H, 7.0	74.39 7.02	2 990, 1 685, 1 300, 1 250 730
(5c-en)	84—85	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	C, 74.5 H, 7.1	74.39 7.02	2 980, 1 690, 1 240, 1 140 740
(5c-ex)	94—96	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	C, 74.4 H, 7.15	74.39 7.02	2 950, 1 690, 1 250, 1 150 750
(5d-en)	129—130	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub>	C, 75.65 H, 6.55	75.53 6.71	2 950, 1 685, 1 250, 730
(5e-en)	99—100	C <sub>16</sub> H <sub>20</sub> O <sub>3</sub>	C, 76.3 H, 7.1	76.03 7.09	2 930, 1 680, 1 590, 1 260 1 200, 980, 720
(5f-en)	113—114	C <sub>16</sub> H <sub>20</sub> O <sub>3</sub>	C, 76.4 H, 7.4	76.48 7.43	2 900, 1 690, 1 240, 1 140 730
(5h-ex)	103—104	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	C, 78.8 H, 6.3	78.72 6.29	3 050, 1 690, 1 590, 1 150 740
(5i-en)	89—90	C <sub>20</sub> H <sub>18</sub> O <sub>3</sub>	C, 78.45 H, 5.95	78.41 5.92	2 950, 1 690, 1 590, 1 150 740
(5i-ex)	95	C <sub>20</sub> H <sub>18</sub> O <sub>3</sub>	C, 78.15 H, 5.95	78.41 5.92	2 950, 1 685, 1 600, 1 140 750
(5q-en)	121—122	C <sub>16</sub> H <sub>16</sub> O <sub>5</sub>	C, 66.6 H, 5.6	66.66 5.59	2 950, 1 740, 1 700, 1 260 740
(5q-ex)	131—132	C <sub>16</sub> H <sub>16</sub> O <sub>5</sub>	C, 66.65 H, 5.6	66.66 5.59	2 880, 1 730, 1 690, 1 275 740
(5r-en)	106—107	C <sub>17</sub> H <sub>18</sub> O <sub>5</sub>	C, 67.6 H, 6.1	67.54 6.00	2 950, 1 730, 1 680, 1 590, 1 270, 1 140, 980
(5r-ex)	113—114	C <sub>17</sub> H <sub>18</sub> O <sub>5</sub>	C, 67.55 H, 6.0	67.54 6.00	2 990, 1 720, 1 680, 1 600 1 250, 1 140, 740
(5s-en)	142—143	C <sub>16</sub> H <sub>13</sub> O <sub>3</sub> N	C, 70.6 H, 5.15 N, 5.5	70.58 5.13 5.41	2 990, 2 240, 1 685, 1 590 1 275, 1 140, 980, 740
(5t-en)	170 *	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N	C, 71.2 H, 5.7 N, 5.15	71.36 5.61 5.20	2 990, 2 250, 1 700, 1 595 1 140, 990, 740
(5u-en)	108—109	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.1 H, 6.7	70.05 6.61	2 990, 1 690, 1 590, 1 290 1 140
(5u-ex)	77—79	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.05 H, 6.7	70.05 6.61	2 990, 1 700, 1 595, 1 290, 1 150, 1 110
(5v-en)	89—91	C <sub>17</sub> H <sub>20</sub> O <sub>4</sub>	C, 71.0 H, 7.05	70.81 6.99	2 990, 1 700, 1 595, 1 280 720
(5v-ex)	91—92	C <sub>17</sub> H <sub>20</sub> O <sub>4</sub>	C, 70.85 H, 6.95	70.81 6.99	2 990, 1 700, 1 595, 1 280 1 150
(5w)	86	C <sub>18</sub> H <sub>22</sub> O <sub>5</sub>	C, 67.65 H, 6.7	67.91 6.97	2 990, 1 695, 1 595, 1 445 1 275, 1 170
(5x)	48—50	C <sub>16</sub> H <sub>14</sub> O <sub>3</sub> S	C, 67.05 H, 5.0 S, 11.35	67.11 4.93 11.20	2 940, 1 680, 1 675, 1 590, 1 250, 740

\* Sublimed.

(OH), and 7.5—7.8 (m, 4 H) (Found: C, 73.75; H, 7.78. C<sub>16</sub>H<sub>20</sub>O<sub>3</sub> requires C, 73.82; H, 7.73%).

*Reduction of E-(7h) with NaBH<sub>4</sub>.*—The alkylidene-phthalide E-(7h) (100 mg), dissolved in methanol (20 ml), was reduced with NaBH<sub>4</sub>. The reaction mixture was stirred for 2 h at room temperature, poured into water, and extracted twice with ether. Purification by chromatography on silica gel yielded E-(9h) (78 mg, 78%).

(E)-3(4-Hydroxy-1,3-dimethyl-3-phenylpentylidene)-phthalide E-(9h): m.p. 153—154 °C,  $\nu_{\max.}$  (KBr) 3 440 (OH), 2 960, 1 740 (phthalide C=O), 1 275, 1 090, 760, and 690 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.18 (d, *J* 7 Hz, 3 H), 1.34 (s, 3 H), 1.58 (s, 3 H), 3.02 and 3.34 (ABq, *J* 15 Hz, 2 H), 4.04 (q, *J* 7 Hz, 1 H), and 7.2—7.9 (m, 9 H) (Found: C, 78.1; H, 6.8. C<sub>21</sub>H<sub>22</sub>O<sub>3</sub> requires C, 78.23; H, 6.88%).

*Acetylation of the Tetracyclic Compound (11l).*—A solution of (11l) (100 mg) in acetic anhydride (20 ml) was cooled to -20 °C, and three drops of HClO<sub>4</sub> were added carefully; immediately the mixture was poured into ice-water (100 ml). The reaction mixture was extracted with two portions of CH<sub>2</sub>Cl<sub>2</sub> and the organic extracts were washed with water.

Removal of the solvent on a rotary evaporator gave a yellow oil, which was separated by column chromatography on silica gel to yield (5l'-en) (91 mg, 78%).

7 $\beta$ -Acetoxymethyl-6,9-dimethyl-6,7,8,9-tetrahydro-6 $\alpha$ ,9 $\alpha$ -epoxybenzocyclo-octene-5,10-dione (5l'-en); m.p. 96—98 °C;  $\nu_{\max.}$  (KBr) 2 980, 1 745, (ester C=O), 1 690 (conjugated C=O), 1 220, and 770 cm<sup>-1</sup>;  $\delta$ (CDCl<sub>3</sub>) 1.60 (s, 6H), 1.63 (s, 3 H, CO-Me), 2.2 (m, 1 H), 2.6 (m, 2 H), 4.16 (m, 2 H), and 7.5—7.9 (m, 4 H); <sup>13</sup>C n.m.r.  $\delta$ (CDCl<sub>3</sub>) 19.7 (q), 24.3 (q), 24.9 (q), 40.1 (t), 48.2 (d), 61.9 (t), 88.7 (s), 90.3 (s), 128.7 (d), 132.5 (d), 132.7 (d), 134.3 (s), 135.5 (s), 169.5 (s), 205.4 (s), and 206.4 (s) (Found: C, 67.5; H, 6.1. C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> requires C, 67.54; H, 6.00%).

*Transformation of the Tetracyclic Compound (11l) into the Primary Adduct (5q-en).*—A solution of (11l) (100 mg) in acetone (20 ml) was cooled in ice, and Jones reagent (2.0 m) was added dropwise with vigorous stirring until a red colour persisted. The reaction mixture was stirred at 30 °C for 24 h. The excess of oxidant was destroyed with isopropyl alcohol. Water was added to dissolve the precipitated salts, and the resulting green solution was extracted twice

TABLE 6  
<sup>1</sup>H N.m.r. (CDCl<sub>3</sub>, δ) of the primary adducts (5)

Compd.	Me <sup>1</sup> , Me <sup>2</sup>	H <sub>arom.</sub>	H <sub>others</sub>
(5a)	1.43	7.5—7.8 (m, 2 H)	1.09 (s, 3 H), 1.25 (s, 3 H), 1.92 and
	1.66	7.8—8.1 (m, 2 H)	2.15 (ABq, <i>J</i> 14 Hz, 2 H)
(5b)	1.55	7.5—7.7 (m, 2 H)	1.10 (d, <i>J</i> 7 Hz, 3 H), 1.20 (d, <i>J</i> 7 Hz, 3
	1.63	7.7—8.1 (m, 2 H)	H), 1.7—1.9 (m, 2 H)
(5c-en)	1.57	7.5—7.7 (m, 2 H)	0.90 (d, <i>J</i> 7 Hz, 6 H), 2.40 (m, 2 H)
		7.7—8.0 (m, 2 H)	
(5c-ex)	1.42	7.5—7.8 (m, 2 H)	1.13 (d, <i>J</i> 7 Hz, 6 H), 2.55 (m, 2 H)
		7.8—8.1 (m, 2 H)	
(5d-en)	1.62	7.6—8.0 (m, 4 H)	1.1—1.8 (m, 6 H), 2.9 (m, 2 H)
(5e-en)	1.52	7.6—7.7 (m, 2 H)	1.1—1.8 (m, 8 H), 2.3 (m, 2 H)
		7.8—7.7 (m, 2 H)	
(5f-en)	1.60	7.5—7.7 (m, 2 H)	1.0—2.0 (m, 10 H), 2.5 (m, 2 H)
		7.8—7.9 (m, 2 H)	
(5h-ex)	1.03	7.5—7.7 (m, 2 H)	1.3 (s, 3 H), 2.50 and 2.93 (ABq, <i>J</i> 13 Hz,
		7.7—7.8 (m, 2 H)	2 H), 7.2—7.5 (m, 5 H)
(5i-en)	1.60	7.5—8.0 (m, 4 H)	2.10 (dd, <i>J</i> 4 and 12 Hz, 1 H), 2.85 (dd,
			<i>J</i> 8 and 12 Hz, 1 H), 3.60 (dd, <i>J</i> 4 and
(5i-ex)	1.13	7.5—7.9 (m, 4 H)	8 Hz, 1 H), 7.0—7.4 (m, 5 H)
			2.30 (dd, <i>J</i> 10 and 15 Hz, 1 H), 2.73 (dd,
(5q-en)	1.64	7.7—8.0 (m, 4 H)	8 and 15 Hz, 1 H), 3.63 (dd, <i>J</i> 8 and 10
			Hz, 1 H), 7.2—7.3 (m, 5 H)
(5q-ex)	1.73	7.7—7.8 (m, 4 H)	2.35 (dd, <i>J</i> 6 and 12 Hz, 1 H), 2.68 (dd,
			<i>J</i> 8 and 12 Hz, 1 H), 3.20 (dd, <i>J</i> 6 and
(5r-en)	1.53	7.6—7.7 (m, 2 H)	8 Hz, 1 H), 3.67 (s, 3 H)
			2.40 (dd, <i>J</i> 4 and 14 Hz, 1 H), 2.53 (dd,
(5r-ex)	1.60	7.8—8.0 (m, 2 H)	<i>J</i> 8 and 14 Hz, 1 H), 3.38 (dd, <i>J</i> 4 and 8
			Hz, 1 H), 3.80 (s, 3 H)
(5s-en)	1.47	7.5—7.8 (m, 4 H)	1.52 (s, 3 H), 1.66 and 2.00 (ABq, <i>J</i> 14
			Hz, 2 H), 3.70 (s, 3 H)
(5t-en)	1.60	7.6—7.8 (m, 2 H)	1.25 (s, 3 H), 2.13 and 2.98 (ABq, <i>J</i>
			13 Hz, 2 H), 3.73 (s, 3 H)
(5u-en)	1.70	7.6—7.8 (m, 2 H)	2.43 (m, 2 H), 3.52 (dd, <i>J</i> 4 and 6 Hz,
			1 H)
(5u-ex)	1.70	7.8—8.0 (m, 2 H)	1.50 (s, 3 H), 2.14 and 2.76 (ABq, <i>J</i> 15
			Hz, 2 H)
(5v-en)	1.73	7.6—7.8 (m, 2 H)	0.74 (t, <i>J</i> 7 Hz, 3 H), 1.90 (dd, <i>J</i> 6 and 13
			Hz, 1 H), 2.70 (d, <i>J</i> 13 Hz, 1 H), 3.30 (d,
(5v-ex)	1.76	7.8—8.1 (m, 2 H)	<i>J</i> 6 Hz, 1 H), 3.24 (m, 2 H)
			1.23 (t, <i>J</i> 6 Hz, 3 H), 2.03 (dd, <i>J</i> 4 and 15
(5w-en)	1.53	7.5—7.8 (m, 2 H)	Hz, 1 H), 2.38 (dd, <i>J</i> 7 and 15 Hz, 1 H),
			3.56 (m, 2 H), 4.00 (dd, <i>J</i> 4 and 7 Hz,
(5w-ex)	1.58	7.9—8.1 (m, 2 H)	1 H)
			0.63 (t, <i>J</i> 7 Hz, 3 H), 1.36 (s, 3 H)
(5x-en)	1.45	7.5—7.6 (m, 2 H)	1.63 and 2.92 (ABq, <i>J</i> 16 Hz, 2 H)
			1.23 (t, <i>J</i> 7 Hz, 3 H), 1.28 (s, 3 H), 1.90
(5x-ex)	1.45	7.8—8.0 (m, 2 H)	and 2.43 (ABq, <i>J</i> 14 Hz, 2 H)
			0.76 (t, <i>J</i> 7 Hz, 3 H), 1.20 (t, <i>J</i> 7 Hz,
(5y-en)	1.52	7.6—7.8 (m, 2 H)	3 H), 1.90 and 2.90 (ABq, <i>J</i> 10 Hz, 2 H),
			3.1—3.9 (m, 4 H)
(5y-ex)	1.62	7.8—8.1 (m, 2 H)	3.98 (m, 1 H), 4.67 (d, <i>J</i> 10 Hz, 1 H),
			5.51 (dd, <i>J</i> 3 and 6 Hz, 1 H), 6.27 (dd,
(5z-en)	1.42	7.6—7.7 (m, 2 H)	<i>J</i> 2 and 6 Hz, 1 H)
			7.9—8.0 (m, 2 H)
(5z-ex)	1.50	7.5—7.9 (m, 4 H)	

 TABLE 7  
 Physical properties of the spirophthalides (6)

Compd.	M.p. (°C)	Formula	Found (%)	Required (%)	$\nu_{\max.}/\text{cm}^{-1}$ (KBr)
(6a)	104—105	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	C, 74.25	74.39	2 940, 1 770, 1 470, 1 390
			H, 7.0	7.02	1 280, 1 220, 1 090, 1 040
(6d)	112—114	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub>	C, 75.65	75.53	2 950, 1 770, 1 460, 1 040
			H, 6.75	6.71	
(6h)	137—138	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	C, 78.7	78.72	2 950, 1 765, 1 230, 1 140
			H, 6.2	6.29	965, 750
(6i)	124—126	C <sub>20</sub> H <sub>18</sub> O <sub>3</sub>	C, 78.4	78.41	2 960, 1 770, 1 250, 1 150
			H, 5.8	5.91	740
(6j)	224—226	C <sub>26</sub> H <sub>22</sub> O <sub>3</sub>	C, 81.35	81.65	2 990, 1 770, 1 600, 1 450
			H, 5.65	5.80	1 385, 1 280, 1 225, 1 050
(6q)	107—109	C <sub>16</sub> H <sub>16</sub> O <sub>5</sub>	C, 66.7	66.66	1 775, 1 750, 1 730, 1 390
			H, 5.6	5.59	1 240, 1 035, 765
(6r)	144—145	C <sub>17</sub> H <sub>18</sub> O <sub>5</sub>	C, 67.8	67.54	1 780, 1 740, 1 290, 1 220
			H, 6.2	6.00	1 090, 1 060
(6s)	157—159	C <sub>15</sub> H <sub>13</sub> O <sub>3</sub> N	C, 70.6	70.58	2 950, 2 240, 1 775, 1 285
			H, 5.2	5.13	1 230, 1 080, 1 050
(6t)	202—203	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> N	N, 5.35	5.49	
			C, 71.45	71.36	2 990, 2 240, 1 790, 1 475
			H, 5.75	5.61	1 390, 1 290, 1 230, 1 060
			N, 5.2	5.20	

TABLE 8  
<sup>1</sup>H N.m.r. of the spirophthalides (6) (CDCl<sub>3</sub>, δ)

Compd.	Me <sup>1</sup> , Me <sup>2</sup>	H <sub>arom.</sub>	H <sub>others</sub>
(6a)	1.06 1.38	7.5—8.0 (m, 4 H)	1.16 (s, 3 H), 1.16 (s, 3 H), 1.68 and 2.26 (ABq, <i>J</i> 10 Hz, 2 H)
(6d)	1.18	7.7—8.2 (m, 4 H)	1.4—2.0 (m, 6 H), 3.2 (m, 2 H)
(6h)	0.90 1.34	7.5—8.1 (m, 4 H)	1.90 (s, 3 H), 2.60 and 2.84 (ABq, <i>J</i> 12 Hz, 2 H), 7.3—7.5 (m, 5 H)
(6i)	0.90	7.5—8.2 (m, 4 H)	2.0 (m, 1 H), 2.45 (m, 1 H), 3.60 (m, 1 H) 7.3—7.5 (m, 5 H)
(6j)	1.33 1.24 1.36	7.5—8.0 (m, 4 H)	3.06 and 3.28 (ABq, <i>J</i> 11 Hz, 2 H), 7.3—7.5 (m, 10 H)
(6q)	1.30 1.30	7.5—8.0 (m, 4 H)	2.5 (m, 2 H), 3.44 (dd, <i>J</i> 4 and 6 Hz, 1 H), 3.76 (s, 3 H)
(6r)	1.23 1.39	7.5—7.8 (m, 2 H) 7.8—8.0 (m, 2 H)	1.66 (s, 3 H), 2.32 and 2.70 (ABq, <i>J</i> 12 Hz, 2 H), 3.75 (s, 3 H)
(6s)	1.30 1.52	7.5—8.0 (m, 4 H)	2.28 (dd, <i>J</i> 4 and 12 Hz, 1 H), 2.81 (dd, <i>J</i> 9 and 12 Hz, 1 H), 3.42 (dd, <i>J</i> 4 and 9 Hz, 1 H)
(6t)	1.26 1.37	7.5—8.0 (m, 4 H)	1.76 (s, 3 H), 2.46 and 2.60 (ABq, <i>J</i> 13 Hz, 2 H)

TABLE 9  
 Physical properties of the alkylidene-phthalides (7)

Compound	M.p. (°C)	Formula	Found (%)	Required (%)	$\nu_{\max.}/\text{cm}^{-1}$ (KBr)
Z-(7d)	53—56	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub>	C, 74.35 H, 7.1	74.39 7.02	2 940, 1 765, 1 695, 1 470 1 275, 1 060, 990, 775, 690
E-(7d)	128—129	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub>	C, 74.4 H, 6.9	74.39 7.02	2 960, 1 765, 1 705, 1 475 1 280, 1 050, 970, 695
Z-(7e)	161—162	C <sub>18</sub> H <sub>20</sub> O <sub>3</sub>	C, 76.1 H, 7.1	76.03 7.09	2 920, 1 755, 1 705, 1 275, 1 215, 760
E-(7e)	129—130	C <sub>18</sub> H <sub>20</sub> O <sub>3</sub>	C, 76.05 H, 7.2	76.03 7.09	2 940, 1 765, 1 705, 1 275, 1 060, 755
Z-(7f)	118—119	C <sub>19</sub> H <sub>22</sub> O <sub>3</sub>	C, 76.4 H, 7.5	76.48 7.43	2 990, 1 775, 1 700, 1 480, 1 280, 1 070, 770, 700
E-(7f)	124—125	C <sub>19</sub> H <sub>22</sub> O <sub>3</sub>	C, 76.55 H, 7.4	76.48 7.43	2 940, 1 770, 1 710, 1 050 770, 700
Z-(7h)	152—153	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	C, 78.5 H, 6.3	78.72 6.29	1 770, 1 705, 1 230, 1 180
E-(7h)	194—195	C <sub>21</sub> H <sub>20</sub> O <sub>3</sub>	C, 78.7 H, 6.05	78.72 6.29	2 980, 1 760, 1 705, 1 270 1 190
Z-(7i)	111—112	C <sub>20</sub> H <sub>18</sub> O <sub>3</sub>	C, 78.25 H, 5.95	78.41 5.92	1 770, 1 720, 1 285, 1 100 770, 700
E-(7i)	129—130	C <sub>20</sub> H <sub>18</sub> O <sub>3</sub>	C, 78.35 H, 6.0	78.41 5.92	1 775, 1 715, 1 480, 1 275 770, 700
Z-(7j)	143—144	C <sub>20</sub> H <sub>22</sub> O <sub>3</sub>	C, 81.7 H, 5.9	81.65 5.80	1 770, 1 700, 1 095, 1 080 705
E-(7j)	169—170	C <sub>20</sub> H <sub>22</sub> O <sub>3</sub>	C, 81.65 H, 5.85	81.65 5.80	1 765, 1 700, 1 465, 1 065 705
Z-(7l)	97—99	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub>	C, 69.3 H, 6.25	69.21 6.20	3 400, 1 770, 1 700, 1 090 700
E-(7l)	114—115	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub>	C, 69.25 H, 6.3	69.21 6.20	3 300, 1 760, 1 690, 1 180 720
Z-(7n)	87—89	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.1 H, 6.25	70.05 6.20	3 420, 1 775, 1 695, 1 100 720
E-(7n)	95—97	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.1 H, 6.65	70.05 6.61	3 420, 1 775, 1 695, 1 090 720
Z-(7o)	78—79	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.15 H, 6.8	70.05 6.61	3 400, 1 765, 1 700, 1 100 730
E-(7o)	86—88	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.0 H, 6.8	70.05 6.61	3 450, 1 755, 1 705, 1 105 730
Z-(7q)	95—96	C <sub>16</sub> H <sub>16</sub> O <sub>5</sub>	C, 66.8 H, 5.5	66.66 5.59	1 770, 1 720, 1 290, 1 100 780, 700
E-(7q)	114—115	C <sub>16</sub> H <sub>16</sub> O <sub>5</sub>	C, 66.7 H, 5.65	66.66 5.59	1 765, 1 720, 1 290, 1 080 780, 700
Z-(7r)	118—120	C <sub>17</sub> H <sub>18</sub> O <sub>5</sub>	C, 67.5 H, 6.05	67.54 6.00	2 940, 1 765, 1 710, 1 290 1 245, 1 000, 990, 770, 690
E-(7r)	97—98	C <sub>17</sub> H <sub>18</sub> O <sub>5</sub>	C, 67.65 H, 6.05	67.54 6.00	2 950, 1 775, 1 720, 1 245 1 110, 780
Z-(7s)	116—117	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> N	C, 70.4 H, 5.25 N, 5.45	70.58 5.13 5.49	2 250, 1 770, 1 700, 1 250 740
E-(7s)	109—110	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> N	C, 70.5 H, 5.2 N, 5.45	70.58 5.49 5.49	2 240, 1 775, 1 695, 1 240 750
Z-(7t)	102—103	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N	C, 71.45 H, 5.45 N, 5.05	71.39 5.61 5.20	3 000, 2 240, 1 775, 1 735 1 290, 1 090, 780, 695
E-(7t)	128—129	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N	C, 71.35 H, 5.8 N, 5.05	71.36 5.61 5.20	3 000, 2 250, 1 775, 1 730, 1 280, 1 090, 1 050, 780
Z-(7v)	89—90	C <sub>17</sub> H <sub>20</sub> O <sub>4</sub>	C, 70.9 H, 7.05	70.81 6.99	2 990, 1 765, 1 720, 1 480 1 280, 1 110, 1 050, 780, 760
E-(7v)	91—92	C <sub>17</sub> H <sub>20</sub> O <sub>4</sub>	C, 70.9 H, 7.05	70.81 6.99	3 000, 1 765, 1 720, 1 100 785, 700

TABLE 10  
<sup>1</sup>H N.m.r. of the alkylidenephthalides (7) (CDCl<sub>3</sub>, δ)

Compd.	Me <sup>1</sup> , Me <sup>2</sup>	H <sub>arom.</sub>	H <sub>others</sub>
Z-(7d)	2.03 2.07	7.5—8.0 (m, 4 H)	1.5—2.2 (m, 6 H), 3.4 (m, 1 H), 3.9 (m, 1 H)
E-(7d)	1.95 2.00	7.5—8.0 (m, 4 H)	1.7—2.1 (m, 6 H), 3.4 (m, 1 H), 3.9 (m, 1 H)
Z-(7e)	2.08 2.08	7.4—7.7 (m, 2 H) 7.8—8.0 (m, 2 H)	1.4—2.2 (m, 8 H), 3.0—3.2 (m, 2 H)
E-(7e)	2.05 2.10	7.3—7.9 (m, 4 H)	1.2—2.2 (m, 8 H), 3.1—3.2 (m, 2 H)
Z-(7f)	2.05 2.06	7.4—8.0 (m, 4 H)	1.2—2.2 (m, 10 H), 3.2 (m, 1 H), 3.9 (m, 1 H)
E-(7f)	1.98 2.06	7.4—8.0 (m, 4 H)	1.2—2.2 (m, 10 H), 3.1 (m, 1 H), 3.8 (m, 1 H)
Z-(7h)	1.60 1.98	7.4—7.7 (m, 3 H) 7.9 (m, 1 H)	1.60 (s, 3 H), 2.88 and 3.58 (ABq, <i>J</i> 12 Hz, 2 H), 7.3 (m, 5 H)
E-(7h)	1.64 1.99	7.4—8.0 (m, 4 H)	1.60 (s, 3 H), 2.90 and 3.76 (ABq, <i>J</i> 14 Hz, 2 H), 7.2—7.4 (m, 5 H)
Z-(7i)	1.93 2.06	7.4—8.0 (m, 4 H)	2.6—3.3 (m, 2 H), 4.08 (dd, <i>J</i> 6 and 8 Hz, 1 H), 7.3 (m, 5 H)
E-(7i)	1.91 2.10	7.4—8.0 (m, 4 H)	2.83 (dd, <i>J</i> 8 and 14 Hz, 1 H), 3.38 (dd, <i>J</i> 6 and 14 Hz, 1 H), 3.90 (ddm, <i>J</i> 6 and 8 Hz, 1 H), 7.2 (m, 5 H)
Z-(7j)	1.85 2.05	7.4—7.8 (m, 4 H)	3.63 (s, 2 H), 7.1—7.4 (m, 10 H)
E-(7j)	1.75 2.03	7.4—8.0 (m, 4 H)	3.65 (s, 2 H), 7.0—7.4 (m, 10 H)
Z-(7l)	2.20 2.25	7.4—8.0 (m, 4 H)	2.5—3.2 (m, 3 H), 3.84 (d, <i>J</i> 5 Hz, 2 H)
E-(7l)	2.08 2.28	7.3—8.0 (m, 4 H)	2.7—3.0 (m, 3 H), 3.85 (d, <i>J</i> 5 Hz, 2 H)
Z-(7n)	2.16 2.30	7.5—8.0 (m, 4 H)	1.21 (s, 3 H), 2.79 (s, 2 H), 3.66 (s, 2 H)
E-(7n)	2.09 2.20	7.5—8.0 (m, 4 H)	1.24 (s, 3 H), 2.92 (s, 2 H), 3.78 (s, 2 H)
Z-(7o)	2.17 2.25	7.5—8.0 (m, 4 H)	1.26 (d, <i>J</i> 7 Hz, 3 H), 2.7—3.2 (m, 2 H), 3.84 (d, <i>J</i> 6 Hz, 2 H)
E-(7o)	2.04 2.21	7.4—7.9 (m, 4 H)	1.22 (d, <i>J</i> 7 Hz, 3 H), 2.9—3.3 (m, 2 H), 3.76 (d, <i>J</i> 7 Hz, 2 H)
Z-(7q)	2.18 2.29	7.5—8.0 (m, 4 H)	3.00 (m, 2 H), 3.74 (s, 3 H), 3.87 (t, <i>J</i> 6 Hz, 2 H)
E-(7q)	2.05 2.28	7.4—8.0 (m, 4 H)	3.13 (d, <i>J</i> 6 Hz, 2 H), 3.67 (s, 3 H), 3.81 (t, <i>J</i> 6 Hz, 1 H)
Z-(7r)	2.13 2.22	7.4—7.9 (m, 4 H)	1.40 (s, 3 H), 3.1 (m, 2 H)
E-(7r)	1.94 2.22	7.4—8.0 (m, 4 H)	3.78 (s, 3 H)
Z-(7s)	2.27 2.45	7.3—8.0 (m, 4 H)	1.36 (s, 3 H), 3.13 and 3.40 (ABq, <i>J</i> 15 Hz, 2 H), 3.73 (s, 3 H)
E-(7s)	2.28 2.45	7.3—8.0 (m, 4 H)	2.78 (dd, <i>J</i> 9 and 13 Hz, 1 H), 3.15 (dd, <i>J</i> 5 and 13 Hz, 1 H), 3.85 (dd, <i>J</i> 5 and 9 Hz, 1 H)
Z-(7t)	2.30 2.48	7.3—8.0 (m, 4 H)	3.00 (m, 2 H), 4.80 (dd, <i>J</i> 5 and 7 Hz, 1 H)
E-(7t)	2.23 2.53	7.3—8.0 (m, 4 H)	1.58 (s, 3 H), 2.90 and 3.15 (ABq, <i>J</i> 15 Hz, 2 H)
Z-(7v)	2.20 2.23	7.3—7.9 (m, 4 H)	1.55 (s, 3 H), 2.95 and 3.28 (ABq, <i>J</i> 15 Hz, 2 H)
E-(7v)	2.14 2.25	7.3—7.9 (m, 4 H)	1.18 (t, <i>J</i> 7 Hz, 3 H), 1.33 (s, 3 H), 2.68 and 3.03 (ABq, <i>J</i> 14 Hz, 2 H), 3.3 (m, 2 H)
			1.20 (t, <i>J</i> 7 Hz, 3 H), 1.30 (s, 3 H), 2.90 (s, 2 H), 3.4 (m, 2 H)

 TABLE 11  
 Physical properties of the tetracyclic compounds (11)

Compd.	M.p. (°C)	Formula	Found (%)	Required (%)	$\nu_{\max.}/\text{cm}^{-1}$ (KBr)
(11l)	183—184	C <sub>15</sub> H <sub>16</sub> O <sub>4</sub>	C, 69.1 H, 6.2	69.12 6.20	3 310, 2 990, 1 700, 1 260 1 120, 990
(11m)	198 *	C <sub>17</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.8 H, 7.1	70.81 6.99	3 440, 2 980, 1 700, 1 370 1 105, 1 065
(11n)	186—188	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.05 H, 6.75	70.05 6.61	3 360, 1 705, 1 280, 1 120 1 050, 1 020, 765
(11o)	148—150	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>	C, 70.1 H, 6.8	70.05 6.61	3 370, 1 700, 1 380, 1 130 1 060, 780
(11p)	214—215	C <sub>16</sub> H <sub>18</sub> O <sub>5</sub>	C, 65.9 H, 6.3	66.19 6.25	3 470, 3 250, 1 665, 1 120 1 050, 760, 700

\* Sealed.

TABLE 12

Compound	<sup>1</sup> H N.m.r. of the tetracyclic compounds (11) (CDCl <sub>3</sub> , δ)		
	Me <sup>1</sup> , Me <sup>2</sup>	H <sub>arom.</sub>	H <sub>othere</sub>
(11l)	1.34 1.50	7.4—7.7 (m, 4 H)	2.30 (m, 2 H), 2.63 (m, 1 H), 3.75 (d, <i>J</i> 8 Hz, 1 H), 4.04 (dd, <i>J</i> 4 and 8 Hz, 1 H)
(11m)	1.42 1.74	7.4—7.7 (m, 4 H)	1.26 (s, 3 H), 1.58 (s, 3 H), 2.03 (dd, <i>J</i> 2 and 12 Hz, 1 H), 2.52 (m, 1 H)
(11n)	1.23 1.28	7.2—7.6 (m, 4 H)	1.13 (s, 3 H), 1.80 and 2.57 (ABq, <i>J</i> 13 Hz, 2 H), 3.57 and 3.73 (ABq, <i>J</i> 10 Hz, 2 H)
(11o)	1.32 1.46	7.3—7.6 (m, 4 H)	1.17 (d, <i>J</i> 6 Hz, 3 H), 2.2—2.6 (m, 2 H), 3.80 and 4.02 (ABq, <i>J</i> 8 Hz, 2 H)
(11p)	1.33 1.50	7.3—7.8 (m, 4 H)	2.6—2.7 (m, 2 H), 3.6—4.0 (m, 4 H)

with ether. The combined extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent on a rotary evaporator afforded crude acid (5q'-en). This was treated with an excess of diazomethane. After standing at room temperature for 30 min, the solvent was removed on a rotary evaporator. The residue was chromatographed on silica gel to yield (5q-en) (83 mg, 78%).

*Methylation of the Alkylidenephthalides Z- and E-(7q).*—A mixture of Z-(7q) (160 mg), K<sub>2</sub>CO<sub>3</sub> (200 mg), and methyl iodide (100 mg) in dry dimethylformamide (20 ml) was refluxed under a nitrogen atmosphere for 2 h. The reaction mixture was poured into water and extracted twice with ether. The organic extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent on a rotary evaporator gave a yellow oil, which was separated by column chromatography on silica gel to yield the alkylidenephthalide Z-(7r) (133 mg, 79%). The E-isomer (100 mg) was similarly alkylated with methyl iodide to yield E-(7r) (90 mg, 86%).

*Transformation of the Tetracyclic Compound (11n) into the Primary Adduct (5r-en).*—A solution of (11n) (100 mg) in acetone (20 ml) was cooled in ice, and Jones reagent 2.0 M was added dropwise with vigorous stirring until a red colour persisted. The reaction mixture was stirred at 30 °C for 24 h. The excess of oxidant was destroyed with isopropyl alcohol. Water was added to dissolve the precipitated salts, and the resulting green solution was extracted twice with ether. The combined extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent on a rotary evaporator afforded crude acid. This was treated with excess of diazomethane in ether. After 30 min at room temperature, the solvent was removed on a rotary evaporator. The residue was chromatographed on silica gel to yield (5r-en) (62 mg, 56%).

*Transformation of the Primary Adduct (5s-en) into the Primary Adduct (5q-en).*—A mixture of (5s-en) (100 mg), 10 ml of 5% aqueous NaOH, and 10 ml of isopropyl alcohol was heated at 50 °C under a nitrogen atmosphere for 4 h. The reaction mixture was acidified with 5% aqueous HCl. The resulting mixture was extracted twice with ether, and the combined extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent on a rotary evaporator afforded crude acid (5q'-en). This was treated with excess of diazomethane. After 30 min at room temperature, the solvent was removed on a rotary evaporator. The residue was chromatographed on silica gel to yield the primary adduct (5q-en) (62 mg, 55%).

*Methylation of the Alkylidenephthalides Z- and E-(7s).*—A mixture of Z-(7s) (100 mg), K<sub>2</sub>CO<sub>3</sub> (200 mg), and methyl iodide (100 mg) in dimethylformamide (20 ml) was refluxed under a nitrogen atmosphere for 2 h. The reaction mixture was poured into water and extracted twice with ether. The

combined extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent on a rotary evaporator gave a yellow oil, which was separated by column chromatography on silica gel to yield the alkylidenephthalide Z-(7t) (76 mg, 72%).

The E-isomer was similarly methylated with MeI-K<sub>2</sub>CO<sub>3</sub> in DMF to give E-(7t) (79 mg, 75%).

*Transformation of the Primary Adduct (5t-en) into the Primary Adduct (5r-en).*—A mixture of (5t-en) (100 mg), 5% aqueous NaOH (10 ml), and isopropyl alcohol (10 ml), was heated at 50 °C under a nitrogen atmosphere for 4 h. The reaction mixture was acidified with 5% aqueous HCl. The resulting mixture was extracted twice with ether, and the combined organic extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent on a rotary evaporator afforded crude acid. This was treated with an excess of diazomethane in ether. After 30 min, the solvent was removed on a rotary evaporator. The residue was chromatographed on silica gel to yield the primary adduct (5r-en) (71 mg, 63%).

*Quantum Yield Determination.*—Valerophenone actinometry was used for quantum yield determination. The 313 nm line was isolated with a solution containing 0.002 M K<sub>2</sub>CrO<sub>4</sub> in a 1% aqueous solution of K<sub>2</sub>CO<sub>3</sub> as a filter. The degree of the reaction was determined by g.c. analysis relative to known concentration of alkane internal standard.

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