Photochemical Reaction of *N*-Methylnaphthalene-1,8-dicarboximide with Alkenes, Dienes, and Furans. Cyclobutane and Oxetane Formation

Yasuo Kubo,* Manami Suto, Sachiko Tojo, and Takeo Araki
Department of Chemistry, Faculty of Science, Shimane University, Matsue, Shimane 690, Japan

Irradiation of benzene solutions of *N*-methylnaphthalene-1,8-dicarboximide (1) in the presence of alkenes (2b—k) and dienes (9a—c) give the cyclobutanes (3b—j), (4c,e,f,h,i), and (10a—c). Stereospecificity of cyclobutane formation was observed in the reaction with *cis*- and *trans*-but-2-ene (2h,i), and some *endo*-selectivity was observed in the reaction with styrene (2f). In contrast, irradiation of benzene solutions of (1) in the presence of *trans*- and *cis*-stilbene (2j,k), 2,5-dimethylbuta-2,4-diene (9d), and furans (14a,b) gave the fragmentation products (7a,b), (8), (13a,b), (16a,b), and (17a,b) arising *via* precursor oxetanes. In fluorescence quenching studies of the alkenes (2a—d) a linear relationship was found for log plots of their Stern-Volmer slopes ($k_q\tau$) and ionization potentials, and the furans (14a) and (9d) showed new emissions, possibly from exciplexes. A tentative mechanistic scheme for the two types of reactions involving two types of exciplexes generated by the reaction of the singlet excited state of (1) and unsaturated compounds is proposed.

In recent years, imide photochemistry has been much investigated[1] and the photoreactions of alicyclic imides, maleimides, and arenedicarboximides (especially phthalimides) with alkenes have been shown to exhibit remarkable differences. Aliphatic imides undergo effective intra-[2] or inter-molecular oxetane formation,[3] illustrating normal $n\pi^*$ carbonyl photoreactivity, and maleimides undergo dimerization[4] and cyclobutane formation.[5] In contrast, phthalimides undergo alcohol-incorporated C–C coupling at the carbonyl carbon (electron transfer reaction)[6] and insertion of the alkene at the C(=O)–N bond of the imide moiety (dihydrobenzazepinedione formation);[7] in only a few cases is oxetane formation seen.[8] Since the effect of arene structure on the photochemistry of arenedicarboximide has been little investigated,[9] we have now studied the effect in such systems of imide ring size and the presence of an extended π-conjugation system. Recently we reported photoreactions of three types of *N*-methylnaphthalenedicarboximides with alkenes in benzene, in which the arene structure played a crucial role in determining the reaction pathway.[10] The predominant reactions of *N*-methylnaphthalene-1,2- and -2,3-dicarboximides with alkenes were (*a*) insertion of the alkene into the C(=O)–N bond of the imide moiety (dihydronaphthoazepinedione formation), and (*b*) addition of the alkene to the C=O bond of the imide moiety (oxetane formation), respectively. This paper describes the details of the photoreaction of *N*-methylnaphthalene-1,8-dicarboximide (1) with a variety of alkenes, dienes, and furans in benzene. In contrast to other naphthalenedicarboximides, the preferred reaction of (1) is found to be cycloaddition to the aromatic C=C bond (cyclobutane formation), accompanied by oxetane formation in some cases, depending on the structure of the unsaturated compounds.

Results and Discussion

Photoreaction of (1) with Alkenes.—As a typical example, a solution of (1) and 2-methylpropene (2b) in benzene was irradiated by light of >320 nm (aqueous CuSO₄ filter). After evaporation of the solvent, the residue was chromatographed on silica gel to give the cyclobutane (3b), resulting from regiospecific addition at the 1,2-position in the naphthalene ring of (1) (Scheme 1). The structure of (3b) was assigned on the basis of its elemental analysis and spectroscopic properties. The i.r. (1 715 and 1 665 cm⁻¹) and ¹³C n.m.r. (two imide carbonyl
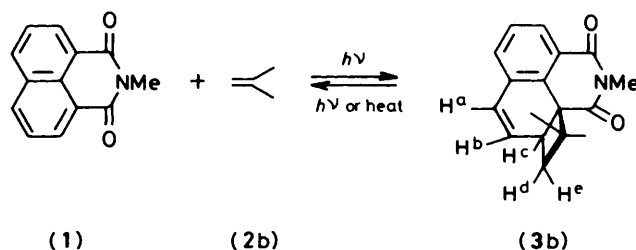
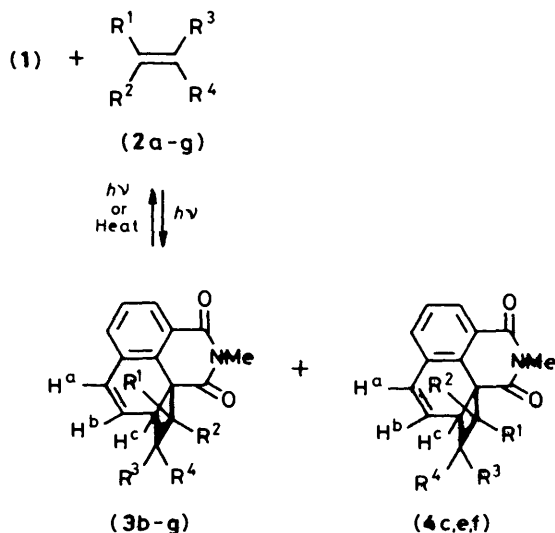**Scheme 1.**

carbons at δ 164.8 and 175.1) spectra clearly demonstrate the presence of the imide skeleton in (3b). The ¹H n.m.r. spectrum of (3b) shows the presence of a *cis*-vinyl group adjacent to a methine carbon (CHᵃ=CHᵇ–CHᶜ; $J_{Hᵃ,Hᵇ}$ 10.3 Hz; $J_{Hᵃ,Hᶜ}$ 1.6 Hz; $J_{Hᵇ,Hᶜ}$ 4.3 Hz). The chemical shifts and coupling constants of Hᵃ—Hᶜ are similar to those of the cyclobutane (5) produced by

(5)
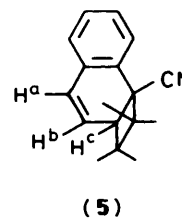
irradiation of 1-cyanonaphthalene and 2,3-dimethylbut-2-ene (2d) ($J_{Hᵃ,Hᵇ}$ 10.1 Hz; $J_{Hᵃ,Hᶜ}$ 2.0 Hz; $J_{Hᵇ,Hᶜ}$ 4.5 Hz).[11] The presence of the coupling between Hᶜ—Hᵉ ($J_{Hᶜ,Hᵈ}$ 10.3 Hz; $J_{Hᶜ,Hᵉ}$ 3.3 Hz) supports the assigned regiochemistry of the cyclobutane (3b), shown in the formula.

The cyclobutane (3b) decomposed to (1) and (2b) in high yield upon irradiation (even by light of >320 nm) and a similar decomposition occurred more slowly in refluxing benzene in the dark. Analogous photodecomposition of cyclobutanes has been previously reported.[11] The course of the reaction between (1) and (2b) upon irradiation at >320 nm was studied by ¹H n.m.r. spectroscopic monitoring of the (3b):(1) ratio; a photo-steady state was reached after 3 h. An approximately linear relationship was observed at the photo-steady state between the concentration of (2b) and the mole ratio of (3b):(1). The ratio was only *ca.* 0.3 in the presence of 1.8M (2b), and a higher

(1) +

(2a-g)

hv
or
Heat ⇅ hv

(3b-g)   +   (4c,e,f)

Scheme 2.

reaction with aliphatic alkenes, appear in the region δ 3.34—3.42. The phenyl (R^1) signals of (3f) (δ 6.7—7.1, m) are shifted to a higher field than those of (4f) (δ 6.7—7.1 and 7.0—7.5), probably owing to the anisotropic shielding effect of the naphthalene ring. The vinyl protons of (3f) (δ 6.18 and 5.98) are also shifted to a higher field than those of (4f) (δ 6.53 and 6.10).

Since the ratio of (3f):(4f) at the photo-steady state (Table 1) might be influenced by the relative rates of photodecomposition for (3f) and (4f), the change with time in the product ratio at the initial stages of the irradiation of (1) and (2f) and that of the photodecomposition, beginning from an equimolar mixture of (3f) and (4f), were examined. In the former case the product ratio was almost identical with that of the photo-steady state and in the latter case no difference in the rates of decomposition between (3f) and (4f) was observed. Hence, we conclude that the product ratio is directly influenced by the endo-selectivity of cyclobutane formation.

The photolysis of (1) in the presence of cis-but-2-ene (2h) and trans-but-2-ene (2i) was carried out in order to clarify the stereochemical course of the reaction. Irradiation of benzene solutions of (1) in the presence of 1.8M (2h) and (2i) gave stereoisomeric mixtures of the cyclobutanes (3h) and (4h)

Table 1. Isolated yields and stabilities of cyclobutanes (3b—g) and (4c,e,f) from the photoreaction of (1) and alkenes (2a—g)[a]

Compd.	R^1	R^2	R^3	R^4	[(2)]/M	Cyclobutane (yield[b]/%)	Stability[c]
(2a)	Bu	H	H	H	1.5	d	
(2b)	Me	Me	H	H	1.8	(3b) (68)	S
(2c)	Me	Me	Me	H	1.4	(3c) and (4c)[e] (73)	U
(2d)	Me	Me	Me	Me	1.2	(3d) (60)	U
(2e)	EtO	H	H	H	1.4	(3e) and (4e)[f] (51)	U
(2f)	Ph	H	H	H	1.2	(3f) (53); (4f) (26)	S
(2g)	Ph	Ph	H	H	1.0	(3g) (67)	S

[a] [(1)]: 36 mM. [b] Yield was based on consumed (1). [c] Thermal stability of the cyclobutane: S = stable at room temperature; U = unstable at room temperature. [d] Not detected. [e] Inseparable mixture of stereoisomers (isomer ratio 2:1). [f] Inseparable mixture of stereoisomers (isomer ratio 4:3).

---

concentration of (1b) was needed to obtain a higher molar ratio of the product (3b):(1).
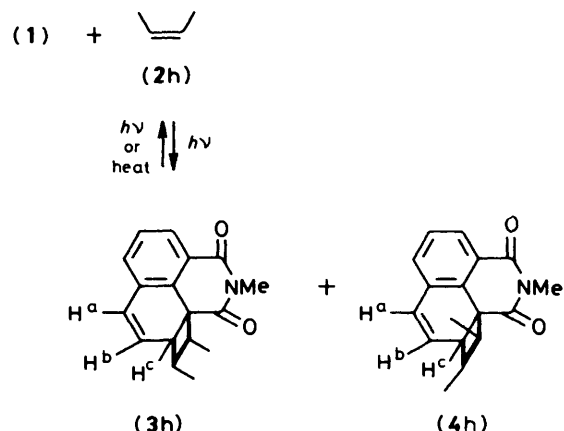
Isolated yields of the cyclobutanes (3b—g) and (4c,e,f), recovered yields of (1), and stabilities of the cyclobutanes are summarized in Table 1 for the photoreactions of (1) in the presence of the alkenes (2a—g). The ^{1}H n.m.r. spectrum of the irradiated mixture of (1) and (2b) indicated no regioisomer of (3b), suggesting high regiospecificity of cyclobutane formation. Table 1 shows cyclobutane formation to be characteristic of the reaction of (1) in the presence of ethylenes substituted with a phenyl group or by more than two alkyl groups.

Irradiation of (1) and hex-1-ene (2a) gave no cyclobutanes but only recovered (1); the reaction with ethyl vinyl ether (2e) gave a mixture of the cyclobutanes (3e) and (4e). The reaction with 2-methylbut-2-enes (2c) and (2e) gave stereoisomeric mixtures of two types of cyclobutanes, (3c) and (4c) and (3e) and (4e). The cyclobutanes (3c) and (4c), (3d), and (3e) and (4e), obtained in reactions with (2c), (2d), and (2e), respectively, were highly unstable and decomposed to the starting materials within 5 h even at room temperature. Other cyclobutanes, (3f,g) and (4f), were also unstable, especially in the liquid state.
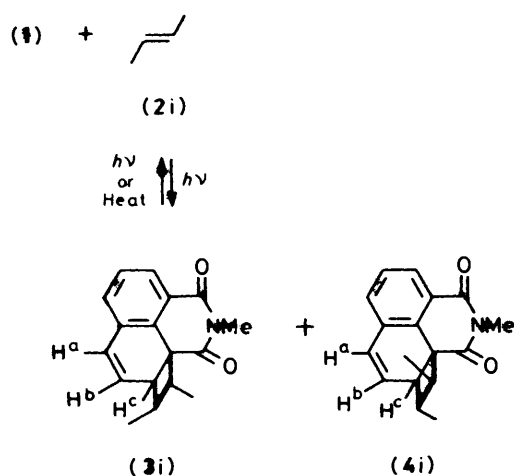
In the reaction with styrene (2f), the two stereoisomeric cyclobutanes (3f) and (4f) were isolated in a molar ratio of 2:1 and their configurations were assigned on the basis of ^{1}H n.m.r. data. In the spectrum of (4f), the NMe signal (δ 2.53) is shifted to a higher field than that of (3f) (δ 3.35), probably owing to the anisotropic shielding effect of the eclipsing phenyl (R^1) ring current. A similar effect was observed in (3g) (δ 3.09). The NMe signals of the cyclobutanes (3b—e) and (4c,e) obtained via the

(isolated yield, 71%) [no (3i) or (4i) was detected in the ^{1}H n.m.r. spectrum of the reaction mixture] and (3i) and (4i) (isolated yield 46%) [no (3h) or (4h)], respectively (Schemes 3 and 4). The reaction with (2i) was considerably slower than that with (2h). The fact that no cis–trans isomerized products were observed upon irradiation of (1) with (2h) and (2i) obviously indicates stereospecificity in the formation of cyclobutane.
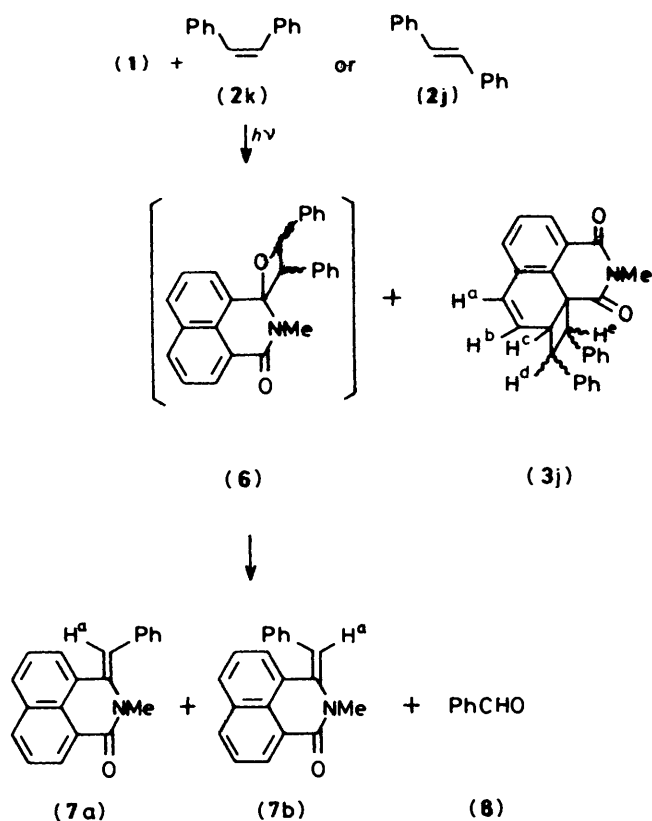
Irradiation of (1) and trans-stilbene (2j) (1M) gave another type of product, (7a) (isolated yield, 43%), (7b) (25%), and

(1)   +

(2h)

hv
or
heat ⇅ hv

(3h)   +   (4h)

Scheme 3.

Scheme 4.

Scheme 5.

Table 2. Isolated yields of cyclobutanes (10a—c) from the photoreaction of (1) with the dienes (9a—c)[a]

Compd.	R[1]	R[2]	Cyclobutane (% yield[b])	Isomer ratio
(9a)	H	H	(10a) (75)	2:1
(9b)	Me	H	(10b) (73)	3:2
(9c)	Me	Me	(10c) (72)	3:1

[a] [(1)]: 36 mM; [(9a—c)]: 1.4 M. [b] Yield was based on consumed (1).

result of the photodecomposition of (3j). The stereochemical course of this reaction was complicated by the concomitant *trans-cis* isomerization of (2j), and was thus poorly characterized. Irradiation of (1) and *cis*-stilbene (2k) (1 M) gave the same products, (3j) (18%), (7a) (44%), (7b) (22%), and (8) (55%), in a similar ratio.

Photoreaction of (1) *with Dienes.*—Buta-1,3-diene (9a), 2-methylbuta-1,3-diene (9b), and 2,3-dimethylbuta-1,3-diene (9c) reacted with (1) to give inseparable stereoisomeric mixtures of the cyclobutanes (10a), (10b), and (10c), respectively. Isolated yields and isomer ratios of the cyclobutanes are shown in Table 2. The cyclobutanes were unstable and decomposed to give the starting materials within 2 days. Hydrogenation of (10a) at room temperature proceeded only at the vinyl moiety to give (11), which was relatively stable under normal conditions (Scheme 6).

Scheme 6.

benzaldehyde (8) (64%), together with a small amount of a mixture of the cyclobutanes (3j) (8%) (Scheme 5). The configurations of (7a) and (7b) were assigned by examining the shielding of the NMe protons in the [1]H n.m.r. spectrum of (7a) (δ 3.09), compared with those of (7b) (δ 3.51); this is probably due to the anisotropic shielding effect of the eclipsing phenyl ring current. The signal for the vinyl proton of (7b) (δ 6.40) is shifted to higher field compared with that of (7a) (δ 6.59). Compounds (7a), (7b), and (8) were considered to arise by fragmentation *via* an oxetane precursor (6), involving carbonyl–alkene metathesis, as previously reported.[12] The product ratio of (7a) + (7b) : (3j) varied with irradiation time, probably as a
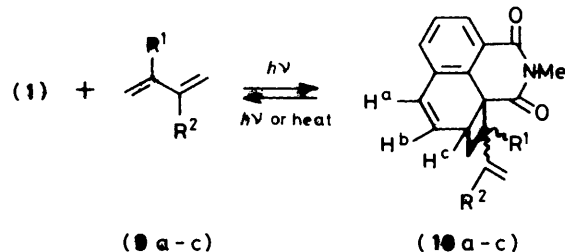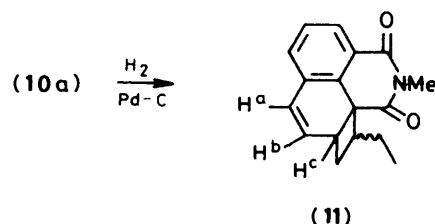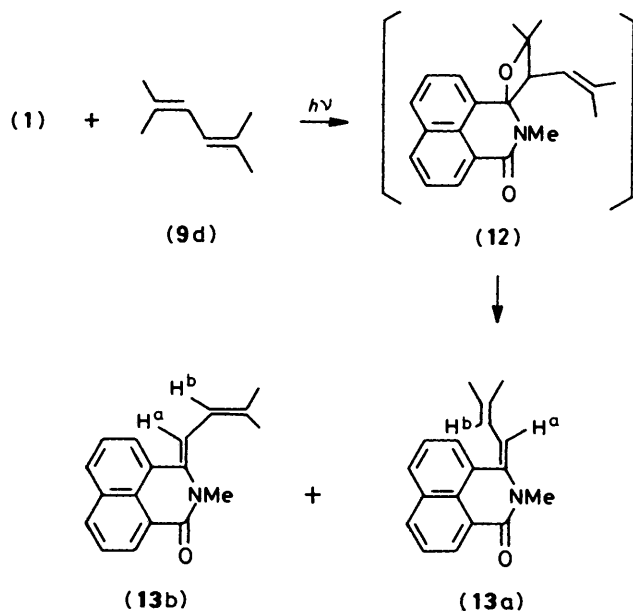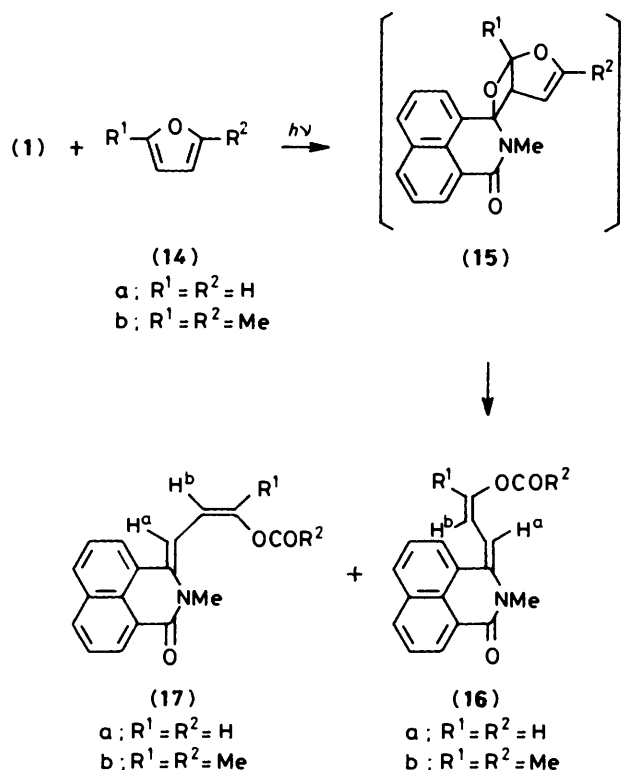
Irradiation of (1) and 2,5-dimethylhexa-2,4-diene (9d) (1.4M) gave a mixture of (13a) and (13b) (total isolated yield 90%, isomer ratio 2.6:1), possibly by fragmentation *via* an oxetane precursor (12) in an analogous manner to the reaction involving (2j) and (2k) (Scheme 7). Only a trace of uncharacterized cyclobutane was detected in the irradiation mixture.

Photoreaction of (1) *with Furans.*—Irradiation of (1) and furan (14a) (1.4M) gave, as a yellow-brown powder, (16a) (49%) and (17a) (41%) (Scheme 8). The structures of the products were assigned on the basis of their elemental analyses and spectroscopic properties. The i.r. spectra showed two kinds of carbonyl bands, corresponding to amide [(16a): 1 665 cm⁻¹; (17a): 1 668 cm⁻¹] and formate [(16a): 1 735 cm⁻¹; (17a): 1 738 cm⁻¹], respectively. The [13]C n.m.r. spectrum of (16a) showed one formate carbon at δ 157 (d) and one amide carbon at δ 160 (s).

(9d)   (12)

(13b)   +   (13a)

Scheme 7.

(14)   (15)

a : $R^1 = R^2 = H$
b : $R^1 = R^2 = Me$

(17)   +   (16)

a ; $R^1 = R^2 = H$ a ; $R^1 = R^2 = H$
b ; $R^1 = R^2 = Me$ b ; $R^1 = R^2 = Me$

Scheme 8.

The ^1H n.m.r. spectra showed formate protons [(16a): δ 8.21; (17a): δ 8.21] and three adjacent vinyl protons [NC=CH^a–CH^b=CR^1(H)OCOR^2(H)] [(16a): δ H^a 6.39, H^b 6.14, R^1 (H) 7.32; (17a): δ H^a 6.50, H^b 6.07, R^1 (H) 7.30], respectively. The coupling constants between H^b and R^1 (H) [(16a): 5.5 Hz; (17a): 5.8 Hz] suggested the Z (cis) configuration of the double bond in both cases.[13] The configuration of the exo-double bond was assigned from the chemical shifts of H^a and H^b. Thus, the H^a signals of (17a) were shifted to slightly lower field than those of

Table 3. Ionization potentials (IP) of alkenes (2a—d)[6c] and Stern-Volmer slopes ($k_q\tau$) from the fluorescence quenching of (1) by the alkenes (2a—d) in benzene[a]

Compd.	IP/V	$k_q\tau/M^{-1}$	log $k_q\tau/M^{-1}$
(2a)	9.46	0.37	−0.437
(2b)	9.23	0.53	−0.275
(2c)	8.68	1.19	0.076
(2d)	8.53	2.02	0.305

[a] [(1)]: 1 × 10^{-5}M; [(2a—d)]: <0.5M; at room temperature; in air-saturated benzene.

(16a), and the H^b signals of (16a) to slightly lower field than those of (17a); this is probably due to the anisotropic shielding effect of the naphthalene ring current. The structure of the products, including the Z configuration of the CH^b=CR^1 double bond, is nicely explained by a fragmentation reaction via the oxetane precursor (15). The regiochemistry of the oxetane formation is analogous to that observed in the photoreaction of other carbonyl compounds with (14a).[14] No other products, including cyclobutanes, were observed (^1H n.m.r.) during the irradiation.

Irradiation of (1) and 2,5-dimethylfuran (14b) (1.3M) slowly gave a mixture of products (16b) and (17b) (total isolated yield 74%, isomer ratio 1 : 1) (Scheme 8). The ^1H n.m.r. and i.r. spectra showed the acetoxy groups (δ 2.00; $\nu_{max.}$ 1 758 cm^{-1}).

Spectroscopic Properties of (1).—The absorption spectrum of (1) in benzene showed strong bands around 348 and 332 nm (log ε 4), which were shifted to longer wavelengths in ethanol. The fluorescence spectrum of (1) was obtained using a dilute benzene solution of (1) (1 × 10^{-5}M) to avoid concentration quenching. The spectrum showed a strong and broad band at $\lambda_{max.}$ 381 nm. The fluorescence excitation spectrum was almost identical with the absorption spectrum. These data suggest that the lowest singlet excited state of (1) is (π,π^*) in character. The energy of the excited singlet state (E_S) estimated from the absorption and fluorescence spectra was 79.4 kcal/mol. A strong phosphorescence band of (1) was observed at $\lambda_{max.}$ 543 nm in EPA (ether isopentane alcohol) (ca. 1 × 10^{-5}M) at 77 K. The long lifetime (1.05 s) suggests that the lowest triplet state is also (π,π^*) in character. The energy of the triplet state (E_T) calculated from the O–O band of the phosphorescence (504 nm) was 56.7 kcal/mol.

Fluorescence Quenching.—Addition of aliphatic alkenes (2a—d) to the air-saturated benzene solutions of (1) (ca. 1 × 10^{-5}M) resulted in a reduction of the fluorescence of (1) without varying the shape and wavelength of the maximum emission. Stern-Volmer plots of the fluorescence quenching by alkenes (2a—d) gave straight lines against the concentration of alkenes (2a—d) up to 0.5M. The Stern-Volmer slopes ($k_q\tau$) are shown in Table 3. Using these values in Table 3, an approximately linear relationship was found between the ionization potentials (IP) of alkenes (2a—d) and log $k_q\tau$. The linear relationship between IP and log $k_q\tau$ indicates an electron donor–acceptor interaction between the excited molecule and the reactant; this is indirect evidence[15] for the intervention of an exciplex in the photochemical cyclobutane formation in the reaction between (1) and alkenes (2a—d). In the present system, the alkenes (2a—d) serve as electron donors in the reaction with the singlet excited state of (1).

The fluorescence quenching behaviour of furan (14a) differs from that of alkenes (2a—d). For instance, as (14a) was added to a benzene solution of (1), the fluorescence of (1) was quenched with broadening of the spectrum over a region of longer
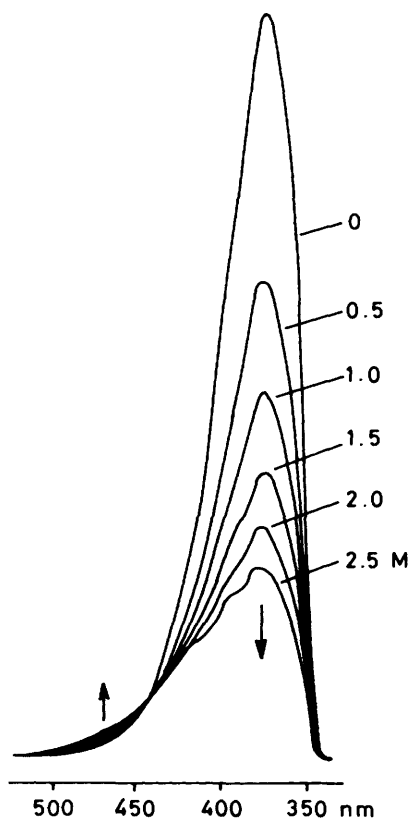
Figure. Fluorescence spectra of benzene solutions of (1) (1 × 10⁻⁵M) in the presence of various concentrations of furan (14a)

wavelengths as shown in the Figure. The appearance of a new emission seems to be a characteristic of exciplex formation[16] between the lowest singlet excited state of (1) and the ground state of (14a). The fact that the photo-products (16a) and (17a) show no emission, and that (1) and (14a) show no charge transfer absorption, supports this concept.

An approximately linear Stern-Volmer plot of the fluorescence quenching by (14a) at concentrations of (14a) up to 0.5M was obtained; the slope $(k_q\tau)$ was 1.17 M⁻¹, which is comparable with that for (2c). A similar new emission was observed when (9d), which also gave fragmentation products via the oxetane, was added to a benzene solution of (1).

Discussion of the Mechanism.—As shown above, two types of photoreaction of (1) with unsaturated compounds, *i.e.* cyclo-butane formation and oxetane formation, were observed, depending on the structure of the unsaturated compounds. On the basis of these results, we propose a tentative mechanistic scheme (Scheme 9), in which unsaturated compounds are denoted as (18).

The most characteristic feature of cyclobutane formation is its stereospecificity, observed in the reactions with (2h) and (2i). In an extreme case, where the lifetime of a biradical such as (25) is long with respect to molecular rotations, the *cis* and *trans* stereochemistry of the alkene will be lost, giving rise to a mixture of four possible products (3h,i) and (4h,i) [in photoreactions with (2h) and (2i), respectively]. Generally, loss of stereochem-istry is observed in reactions arising from the triplet excited state *via* triplet biradicals.[17] The alkene can also react with the singlet excited state of (1) *via* exciplexes or transition states, such as (19) in Scheme 9, which will collapse to cyclobutanes with retention of the stereochemistry. The experimental results of the reactions with (2h) and (2i) support the latter mechanism.

Scheme 9.

(25)
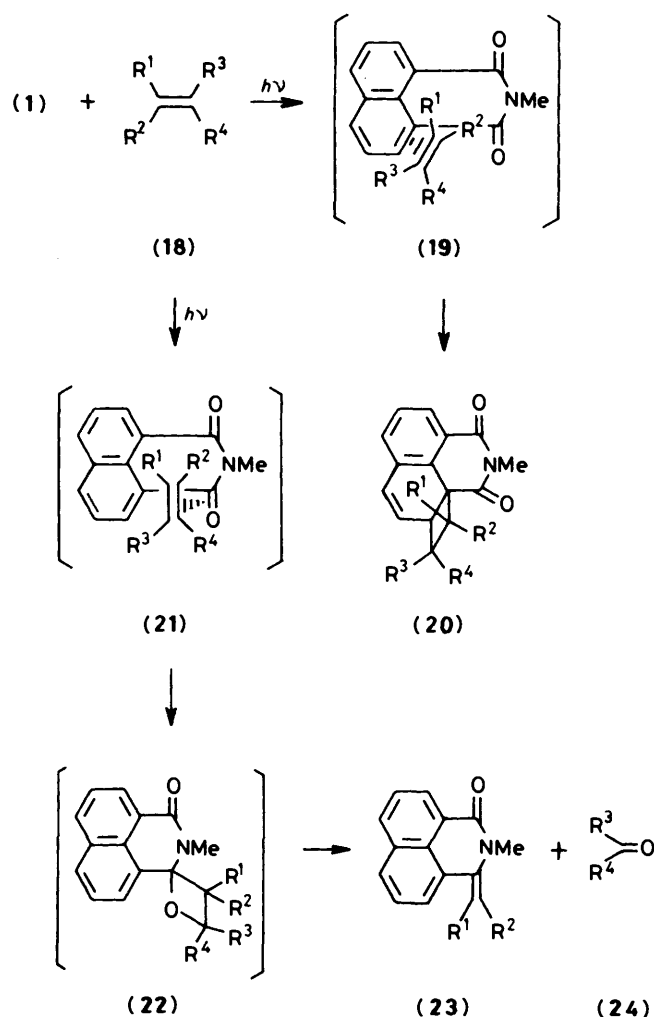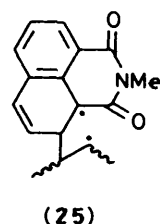
Fluorescence quenching studies indicate that the alkene serves as an electron donor in the reaction with the singlet excited state of (1), and suggest the intervention of exciplexes such as (19) in the cyclobutane formation.

Cyclobutane formation in the present system can be compared with the reactions of cyano aromatic com-pounds.[16c,d,18] This is a better comparison than one with the reaction of maleimides[5] and enones,[17a] since in these cyclo-butane formation occurs from the triplet excited state with-out stereo- or regio-specificity. Cyano aromatic compounds are examples of typical electron acceptors, their reactions proceeding stereospecifically *via* singlet exciplexes in which alkenes act as the electron donor;[18] frequently regioselectivity has also been observed.[18a–c] *endo*-Selectivity, probably a result of stabilization by secondary orbital overlapping in the exciplexes, is also not unknown.[18] The reactions of (1) to give

cyclobutanes were generally regioselective; with (**2f**) some endo-selectivity was also observed.

Oxetane formation is also characteristic of the reactions of (**1**) with unsaturated compounds such as (**18**); such reactions probably proceed via an exciplex such as (**21**) generated by the reaction of the singlet excited state of (**1**) with (**18**) (see Scheme 9). The presence of the exciplex was indicated by fluorescence quenching studies using (**9d**) and (**14a**), both of which gave fragmentation products arising from oxetanes. Comparable $k_q\tau$ values were obtained for (**14a**) and (**2c**), indicating a comparable interaction with the singlet excited state of (**1**). These observations may support the singlet mechanism for oxetane formation. The lowest singlet excited state of (**1**), as well as the triplet, is (π,π^*) in nature. Hence, the oxetane formation will proceed via the (π,π^*) excited state, involving dominant electron donor-acceptor interaction (Scheme 9). Such a process will not be greatly affected by the electronic nature of the lowest excited state, unlike direct oxetane formation from an (n,π^*) excited state. The requirement for dominant electron donor-acceptor interaction has been recognized in oxetane formation from the (π,π^*) excited state.[12,19]

Whether cyclobutane or oxetane (in practice, its fragmentation products) is formed from the reactions of (**1**) with unsaturated compounds depends upon the structure of the latter. For example, oxetane formation was observed only in the reactions with (**2j,k**), (**9d**), and (**14a,b**). A feature shared by (**2j,k**) and (**9d**) is that the former have the lowest ionization (oxidation) potentials of the phenyl substituted ethylenes used, (**2f,g,j,k**), and (**9d**) has the lowest among the dienes (**9a—d**). Furans (**14a,b**) behave quite differently and will not be discussed here.

We can generalize about reaction pathways involving alkenes of lower and higher ionization potentials as follows: (i) a reaction with an unsaturated compound of a lower ionization potential, i.e. a stronger electron donor, will form a more polar exciplex such as (**21**) in which the carbonyl moiety of (**1**) acts as a stronger electron acceptor than the naphthalene moiety, giving rise to the products (**23**) and (**24**) via an oxetane precursor (**22**); (ii) a reaction with an unsaturated compound of a higher ionization potential, i.e. a weaker electron donor, will form a less polar exciplex such as (**19**) at the naphthalene ring, giving rise to the cyclobutane products (**20**).

One of the features most characteristic of the photoreactions of arenedicarboximides (phthalimides, naphthalene-1,2- and 2,3-dicarboximides) has been reported to be the insertion of the alkene into the C(=O)-N bond of the imide moiety (dihydroazepinedione formation).[7,10] However, in the reactions of (**1**) this insertion is almost completely replaced by cyclobutane formation. There are several features common to these two types of reaction: i.e. the reaction occurred with the singlet excited state; it has high stereospecificity and high regiospecificity; and there is a wide variety of unsaturated compounds with which the reaction can occur. Hence, these two types of reaction seem to be closely related in spite of the attacking position being different. Arene structure in the arenedicarboximides seems to play a crucial role in determining the attacking sites, and thus the type of reaction products.

Experimental

M.p.s were measured by a Yanagimoto micromelting point apparatus, and are uncorrected. ^{1}H N.m.r. spectra were determined on a JEOL JNM-MH-100 spectrometer. Chemical shifts are reported in p.p.m. (δ) relative to internal Me$_4$Si. I.r. spectra were obtained with a Hitachi 260-50 spectrophotometer. Mass spectra were measured on a JEOL JMS-DX-300 apparatus. Absorption spectra were recorded on a JASCO UVIDEC-510 spectrophotometer and fluorescence spectra on

a Hitachi 650-10S spectrophotometer. Microanalyses were performed on a Yanagimoto CHN recorder MT-2.

Materials.—N-methylnaphthalene-1,8-dicarboximide (**1**)[20] was prepared by treatment of naphthalene-1,8-dicarboxylic anhydride with methylamine, and purified by chromatography (eluant dichloromethane) and by recrystallization from ethanol. Alkenes (**2a—k**), dienes (**9a—d**), and furans (**14a,b**) were commercially available and purified by distillation (liquid materials) or by recrystallization (solid materials).

Phosphorescence Spectra of (**1**).—Measurements were made using a Hitachi 850 instrument and the spectrum was fully corrected. The phosphorescence spectrum of (**1**) in degassed EPA solution at 77 K showed: (rel. intensity, %) 504 (O–O band, 26), 514 (sh, 28), 538 (sh, 77), 544 (100), 558 (sh, 48), and 590 nm (43).

General Procedure for Irradiation and Product Isolation.—U.v. irradiation of N$_2$ purged benzene solutions (15 ml) containing (**1**) (114 mg; 36 mM) and unsaturated compounds, was carried out with an Eikosha PIH 300-W high-pressure Hg-lamp through an aqueous CuSO$_4$ filter ca. 1 cm in thickness (>420 nm), at ambient temperature. The reactions were monitored by t.l.c. anlayses and ^{1}H n.m.r. measurements. Cyclobutanes, (**1**), and decomposition products from oxetanes showed R_F values of 0.7—0.8, 0.6, and 0.3—0.5, respectively, on t.l.c. (Merck, Kieselgel 60 F$_{254}$), developed by dichloromethane. After evaporation of the solvent, the residue was subjected to column chromatography [Wakogel C-200 (silica gel, 74—149 μ)]. Dichloromethane was used as the eluant for the separation of cyclobutanes from (**1**), and dichloromethane-ether was used for the decomposition products of oxtanes.

Irradiation of (**1**) *and hex-1-ene* (**2a**). Irradiation for 3 days resulted in 93% recovery of (**1**). No products were observed in the ^{1}H n.m.r. spectrum of the irradiation mixture.

Irradiation of (**1**) *and 2-methylpropene* (**2b**). Irradiation gave 2,11,11-trimethyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-dione (**3b**), m.p. 79—81 °C (from ethanol); δ_H(CDCl$_3$) 0.94 (s, 3 H, CMe), 0.97 (s, 3 H, CMe), 1.82 (dd, $J_{H^c.H^e}$ 3.3, $J_{H^d.H^e}$ 13.0 Hz, 1 H, H^e), 2.64 (dd, $J_{H^c.H^d}$ 10.3, $J_{H^d.H^e}$ 13.0 Hz, 1 H, H^d), 3.34 (s, 3 H, NMe), 3.78 (m, 1 H, H^c), 6.11 (dd, $J_{H^b.H^c}$ 4.3, $J_{H^a.H^b}$ 10.6 Hz, 1 H, H^b), 6.49 (dd, $J_{H^a.H^c}$ 1.6, $J_{H^a.H^b}$ 10.6 Hz, 1 H, H^a), 7.1—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_C(CDCl$_3$) 26.5 (q, CMe), 26.6 (q, CMe), 27.0 (q, NMe), 29.8 (d, CH^c), 41.4 (t, H^{d}CH^e), 51.7 (s), 52.1 (s), 123.6 (d), 124.8 (s), 127.1 (d), 127.4 (d), 130.3 (d), 131.2 (s), 132.3 (d), 132.3 (d), 164.8 (s, imide), and 175.1 (s, imide); $\nu_{max.}$(KBr) 1 715 (imide), 1 665 (imide), 1 424, 1 365, 1 292, 1 138, and 763 cm^{-1}; m/z (20 eV) 211 [M^+ of (**1**), 58%], 198 [M^+ − CO of (**1**), base] [probably due to the decomposition to (**1**) under the conditions of the measurement] (Found: C, 76.4; H, 6.4; N, 5.2. C$_{17}$H$_{17}$NO$_2$ requires C, 76.4; N, 6.4; N, 5.2%).

Photochemical and thermal decomposition of (**3b**). Irradiation of a benzene solution (15 ml) of (**3b**) (30 mg) resulted in its decomposition to (**1**) (86% recovered yield). Refluxing of the same solution in the dark for 1 day gave (**1**) in almost quantitative yield.

Irradiation of (**1**) *and 2-methylbut-2-ene* (**2c**). Irradiation gave a stereoisomeric mixture of 2,10,11,11-tetramethyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-dione, (**3c**) and (**4c**) as an oil; δ_H(CDCl$_3$) (major isomer) 0.84 (s, 3 H, CMe), 0.87 (s, 3 H, CMe), 1.09 (d, 3 H, CHMe), 1.6—1.8 (m, 1 H, CHMe), 3.36 (s, 3 H, NMe), 3.6—3.8 (m, 1 H, H^c), 6.26 (dd, 1 H, H^b), 6.54 (d, 1 H, H^a), 7.1—7.4 (m, 2 H, Ar H), and 7.8—8.0 (m, 1 H, Ar H); (minor isomer) 0.73 (s, 3 H, CMe), 0.83 (d, 3 H, CHMe), 0.92 (s, 3 H, CMe), 2.1—2.4 (m, 1 H, CHMe), 3.34 (s, 3 H, NMe), 3.6—3.8 (m, 1 H, H^c), 6.22 (dd, 1 H, H^b), 6.52 (d, 1 H,

H^a), 7.1—7.4 (m, 2 H, Ar H), and 7.8—8.0 (m, 1 H, Ar H); ν_{max} (neat, mixture) 1 717 (imide), 1 666 (imide), 1 419, 1 365, 1 295, 1 142, and 763 cm^{-1}. Because of the instability of the compound, a satisfactory elemental analysis was not obtained. Further purification increased the content of (1). The stereoisomers could not be separated owing to their instability and similar behaviour upon chromatography.

Irradiation of (1) *and* 2,3-*dimethylbut-2-ene* (**2d**). Irradiation gave 2,10,10,11,11-pentamethyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-dione (**3d**) as an oil; δ_H(CDCl$_3$) 0.78 (s, 3 H, CMe), 1.03 (s, 3 H, CMe), 1.08 (s, 3 H, CMe), 1.28 (s, 3 H, CMe), 3.36 (s, 3 H, NMe), 3.99 (dd, 1 H, H^c), 6.29 (dd, 1 H, H^b), 6.61 (dd, 1 H, H^a), 7.1—7.4 (m, 2 H, Ar H), and 7.8—8.0 (m, 1 H, Ar H); ν_{max}(neat) 1 716 (imide), 1 661 (imide), 1 420, 1 363, 1 293, 1 142, and 763 cm^{-1}. Because of the instability of this compound, a satisfactory elemental analysis was not obtained.

Irradiation of (1) *and ethyl vinyl ether* (**2e**). Irradiation gave a stereoisomeric mixture of 11-ethoxy-2-methyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-diones, (**3e**) and (**4e**) as an oil; δ_H(CDCl$_3$) (major isomer) 0.98 (t, 3 H, OCH$_2$*Me*), 1.9—2.2 (m, 1 H), 2.9—3.7 (m, 3 H, C*H*OCH$_2$Me), 3.42 (s, 3 H, NMe), 3.8—4.2 (m, 1 H, H^c), 6.04 (dd, 1 H, H^b), 6.47 (d, 1 H, H^a), 7.1—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_H (minor isomer) 0.73 (t, 3 H, OCH$_2$*Me*), 1.9—2.2 (m, 1 H), 2.9—3.7 (m, 3 H, C*H*OCH$_2$Me), 3.42 (s, 3 H, NMe), 3.8—4.2 (m, 1 H, H^c), 6.04 (dd, 1 H, H^b), 6.44 (d, 1 H, H^a), 7.1—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); ν_{max} (neat, mixture) 1 718 (imide), 1 666 (imide), 1 365, 1 292, 1 095, 1 052, and 764 cm^{-1}. Because of the instability of this compound, a satisfactory elemental analysis was not obtained. The stereoisomers could not be separated owing to this instability and similar behaviour upon chromatography.

Irradiation of (1) *and styrene* (**2f**). Irradiation gave (**3f**) and (**4f**). endo-2-*Methyl*-11-*phenyl*-2,3,3a,4-*tetrahydro*-3a,4-*ethano*-2-*azaphenalene*-1,3-*dione* (**3f**), m.p. 110—113 °C (decomp.); δ_H(CDCl$_3$) 2.3—2.7 (m, 1 H, C*H$_2$*), 2.9—3.3 (m, 1 H, C*H$_2$*), 3.35 (s, 3 H, NMe), 3.7—4.1 (m, 2 H, PhC*H* + H^c), 5.98 (dd, $J_{H^b \cdot H^c}$ 5, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^b), 6.18 (d, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^a), 6.7—7.1 (m, 6 H, ArH), 7.1—7.3 (m, 1 H, ArH), and 7.5—7.7 (m, 1 H, ArH); ν_{max}(KBr) 1 710 (imide), 1 665 (imide), 1 418, 1 360, 1 292, 1 138, and 763 cm^{-1} (Found: C, 80.1; H, 5.35; N, 4.5. C$_{21}$H$_{17}$NO$_2$ requires C, 80.0; N, 5.4; N, 4.4%).

exo-2-*Methyl*-11-*phenyl*-2,3,3a,4-*tetrahydro*-3a,4-*ethano*-2-*azaphenalene*-1,3-*dione* (**3f**), m.p. 105—108 °C (decomp.); δ_H(CDCl$_3$) 2.0—2.3 (m, 1 H, C*H$_2$*), 2.53 (s, 3 H, NMe), 3.3—3.7 (m, 2 H, one of C*H$_2$* + H^c), 4.14 (dd, J_{AB} 7, 9 Hz, 1 H, PhC*H*), 6.10 (dd, $J_{H^b \cdot H^c}$ 3, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^b), 6.53 (d, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^a), 6.7—7.0 (m, 2 H, ArH), 7.1—7.5 (m, 5 H, ArH), and 7.7—8.0 (m, 1 H, ArH); ν_{max}(KBr) 1 713 (imide), 1 665 (imide), 1 422, 1 365, 1 292, 1 140, and 765 cm^{-1} (Found: C, 79.9; H, 5.4; N, 4.3%).

Irradiation of (1) *and* 1,1-*diphenylethylene* (**2g**). Irradiation gave 11,11-*diphenyl*-2-*methyl*-2,3,3a,4-*tetrahydro*-3a,4-*ethano*-2-*azaphenalene*-1,3-*dione* (**3g**), m.p. 171—174 °C (decomp.); δ_H(CDCl$_3$) 2.9—3.2 (m, 1 H, CH$_2$), 3.09 (s, 3 H, NMe), 3.57 (t, 1 H, CH$_2$), 4.9—5.1 (m, 1 H, H^c), 5.66 (dd, $J_{H^b \cdot H^c}$ 5, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^b), 6.17 (d, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^a), 6.8—7.6 (m, 12 H, ArH), and 7.83 (dd, 1 H, ArH); ν_{max}(KBr) 1 720 (imide), 1 668 (imide), 1 416, 1 358, 1 284, and 702 cm^{-1} (Found: C, 82.75; H, 5.3; N, 3.7. C$_{27}$H$_{21}$NO$_2$ requires C, 82.8; N, 5.4; N, 3.6%).

Irradiation of (1) *and* cis-*but-2-ene* (**2h**). Irradiation gave a stereoisomeric mixture of the 2,10,11-trimethyl-3a,4-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-diones, (**3h**) and (**4h**) as an oil; δ_H(CDCl$_3$) (major isomer) 0.72 (d, J 7 Hz, 3 H, CHMe), 0.98 (d, J 7 Hz, 3 H, CH*Me*), 2.3—2.8 (m, 2 H), 3.28 (s, 3 H, NMe), 3.6—3.8 (m, 1 H, H^c), 5.86 (dd, $J_{H^b \cdot H^c}$ 4, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^b), 6.34 (d, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^a), 7.0—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_H (minor isomer) 0.79 (d, J 7 Hz, 3

H, CHMe), 1.24 (d, J 7 Hz, 3 H, CHMe), 1.6—1.8 (m, 1 H), 2.3—2.8 (m, 1 H), 3.29 (s, 3 H, NMe), 3.7—3.9 (m, 1 H, H^c), 5.98 (dd, $J_{H^b \cdot H^c}$ 4, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^b), 6.24 (d, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^a), 7.0—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); ν_{max} (neat, mixture) 1 716 (imide), 1 664 (imide), 1 420, 1 365, 1 295, 1 140, and 765 cm^{-1}. Because of the instability of the compound, a satisfacrory elemental analysis was not obtained. The stereoisomers could not be separated owing to their instability and similar behaviour upon chromatography.

Irradiation of (1) *and* trans-*but-2-ene* (**2i**). Irradiation gave a stereoisomeric mixture of the 2,10,11-trimethyl-3a,4-ethano-2,3,3a,4-tetrahydro-2-azaphenalene-1,3-diones, (**3i**) and (**4i**) as an oil; δ_H(CDCl$_3$) (major isomer) 0.67 (d, J 7 Hz, 3 H, CHMe), 1.25 (d, J 7 Hz, 3 H, CH*Me*), 1.5—1.8 (m, 2 H), 3.27 (s, 3 H, NMe), 3.7—3.9 (m, 1 H, H^c), 6.02 (dd, $J_{H^b \cdot H^c}$ 4, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^b), 6.40 (d, $J_{H^a \cdot H^b}$ 10 Hz, 1 H, H^a), 7.0—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_H (minor isomer) 0.75 (d, J 7 Hz, 3 H, CH*Me*), 1.01 (d, J 7 Hz, 3 H, CH*Me*), 1.5—1.8 (m, 1 H), 2.2—2.6 (m, 1 H), 3.31 (s, 3 H, NMe), 3.7—3.9 (m, 1 H, H^c), 5.96 (dd, 1 H, $J_{H^b \cdot H^c}$ 4, $J_{H^a \cdot H^b}$ 10 Hz, H^b), 6.26 (d, 1 H, $J_{H^a \cdot H^b}$ 10 Hz, H^a), 7.0—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); ν_{max} (neat, mixture) 1 716 (imide), 1 660 (imide), 1 422, 1 365, 1 295, 1 138, and 763 cm^{-1}. Because of the instability of the compound, satisfactory elemental analysis was not obtained. The stereoisomers could not be separated owing to this instability and their similar behaviour upon chromatography.

Irradiation of (1) *in the presence of* trans-*stilbene* (**2j**) *or* cis-*stilbene* (**2k**). Irradiation gave a mixture of cyclobutanes, (**7a**) and (**7b**), and benzaldehyde (**8**). Crystallization of the cyclobutanes (**3j**) from ether gave a pure cyclobutane, the main stereoisomer of 10,11-*diphenyl*-2-*methyl*-2,3,3a,4-*tetrahydro*-3a,4-*ethano*-2-*azaphenalene*-1,3-*dione* (**3j**), m.p. 166—168 °C (decomp.); δ_H(CDCl$_3$) 2.66 (s, 3 H, NMe), 4.18 (m, 1 H, H^c), 4.47 (d, $J_{H^d \cdot H^c}$ 11.7 Hz, 1 H, H^c), 5.09 (dd, $J_{H^c \cdot H^d}$ 9.2, $J_{H^d \cdot H^c}$ 11.7 Hz, 1 H, H^d), 5.67 (dd, $J_{H^b \cdot H^c}$ 3.4, $J_{H^a \cdot H^b}$ 10.0 Hz, 1 H, H^b), 6.45 (d, $J_{H^a \cdot H^b}$ 10.0 Hz, 1 H, H^a), 6.8—7.5 (m, 12 H, ArH), and 7.90 (dd, 1 H, ArH); ν_{max}(KBr) 1 715 (imide), 1 670 (imide), 1 418, 1 360, 1 300, and 756 cm^{-1} (Found: C, 82.9; H, 5.3; N, 3.6. C$_{27}$H$_{21}$NO$_2$ requires C, 82.8; N, 5.4; N, 3.6%).

(Z)-3-*Benzylidene*-2-*methyl*-2,3-*dihydro*-2-*azaphenalen*-1-*one* (**7a**), m.p. 82—85 °C; δ_H(CDCl$_3$) 3.09 (s, 3 H, NMe), 6.59 (s, 1 H, H^a), 7.0—8.0 (m, 10 H, ArH), and 8.34 (m, 1 H, ArH); ν_{max}(KBr) 1 658 (amide), 1 606, 1 448, 1 362, and 783 cm^{-1} (Found: C, 84.0; H, 5.3; N, 5.0. C$_{20}$H$_{15}$NO requires C, 84.2; H, 5.3; N, 4.9%).

(E)-3-*Benzylidene*-2-*methyl*-2,3-*dihydro*-2-*azaphenalen*-1-*one* (**7b**), m.p. 45—50 °C; δ_H(CDCl$_3$) 3.51 (s, 3 H, NMe), 6.40 (s, 1 H, H^a), and 7.0—8.2 (m, 11 H, ArH); ν_{max}(KBr) 1 662 (amide), 1 604, 1 440, 1 360, and 790 cm^{-1} (Found: C, 84.3; H, 5.4; N, 5.0%).

Irradiation of (1) *and* buta-1,3-*diene* (**9a**). Irradiation gave a stereoisomeric mixture of 2-methyl-11-vinyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-dione (**10a**) as an oil; δ_H(CDCl$_3$) (major isomer) 1.9—2.2 (m, 2 H), 3.35 (s, 3 H, NMe), 2.8—4.0 (m, 2 H), 4.4—5.2 (m, 2 H, CH=C*H$_2$*), 5.3—5.9 (m, 1 H, C*H*=CH$_2$), 6.01 (dd, $J_{H^b \cdot H^c}$ 4, $J_{H^a \cdot H^b}$ 11 Hz, 1 H, H^b), 6.34 (d, $J_{H^a \cdot H^b}$ 11 Hz, 1 H, H^a), 7.1—7.3 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_H (minor isomer) 1.9—2.3 (m, 2 H), 3.27 (s, 3 H, NMe), 2.8—4.0 (m, 2 H), 4.4—5.2 (m, 2 H, CH=C*H$_2$*), 5.3—5.9 (m, 1 H, C*H*=CH$_2$), 6.01 (dd, $J_{H^b \cdot H^c}$ 4, $J_{H^a \cdot H^b}$ 11 Hz, 1 H, H^b), 6.44 (d, $J_{H^a \cdot H^b}$ 11 Hz, 1 H, H^a), 7.1—7.3 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); ν_{max} (neat, mixture) 1 718 (imide), 1 668 (imide), 1 475, 1 420, 1 362, and 1 293 cm^{-1}. Because of the instability of the compound, a satisfactory elemental analysis was not obtained. The stereoisomers could not be separated owing to their instability and similar behaviour upon chromatography.

Hydrogenation of (**10a**). To an ethanol solution (20 ml) of (**10a**) (100 mg) was added Pd-C (5 mg, 5%) and the solution

was purged with H_2 (1 atm). After stirring for 1 day at room temperature, the solution was filtered, the solvent evaporated, and the residue subjected to column chromatography (eluant dichloromethane) to give a mixture of stereoisomers of 11-ethyl-2-methyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-dione, (11) (90%); oil; δ_H(CDCl$_3$) (major isomer) 0.82 (t, 3 H, CH$_2$Me), 1.3—1.7 (m, 4 H), 2.2—2.5 (m, 2 H), 3.1—3.4 (m, 1 H), 3.34 (s, 3 H, NMe), 3.6—3.9 (m, 1 H, H^c), 5.96 (dd, 1 H, H^b), 6.54 (d, 1 H, H^a), 7.1—7.5 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_H (minor isomer) 0.82 (t, 3 H, CH$_2$Me), 1.3—1.7 (m, 4 H), 2.2—2.5 (m, 2 H), 3.1—3.4 (m, 1 H), 3.34 (s, 3 H, NMe), 3.6—3.9 (m, 1 H, H^c), 6.30 (dd, 1 H, H^b), 6.58 (d, 1 H, H^a), 7.1—7.5 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); $\nu_{max.}$ (neat, mixture) 1 720 (imide), 1 665 (imide), 1 420, 1 365, 1 295, 1 145, and 765 cm^{-1}. Because of the instability of the compound, a satisfactory elemental analysis was not obtained.

Irradiation of (1) *and* 2-*methylbuta*-1,3-*diene* (9b). Irradiation gave a stereoisomeric mixture of 2,11-dimethyl-11-vinyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-dione, (10b); oil; δ_H(CDCl$_3$) (major isomer) 1.39 (s, 3 H, CMe), 1.8—2.1 (m, 1 H), 2.6—3.1 (m, 1 H, CH$_2$), 3.25 (s, 3 H, NMe), 3.4—3.7 (m, 1 H, H^c), 4.84 (br s, 2 H, C=CH$_2$), 6.06 (dd, $J_{H^b.H^c}$ 4, $J_{H^a.H^b}$ 10 Hz, 1 H, H^b), 6.50 (d, $J_{H^a.H^b}$ 10 Hz, 1 H, H^a), 7.1—7.5 (m, 2 H, ArH), 7.8—8.1 (m, 1 H, ArH); δ_H (minor isomer) 1.39 (s, 3 H, CMe), 1.8—2.1 (m, 1 H), 2.6—3.1 (m, 1 H, CH$_2$), 3.38 (s, 3 H, NMe), 3.4—3.7 (m, 1 H, H^c), 4.68 (br s, 2 H, C=CH$_2$), 6.01 (dd, $J_{H^b.H^c}$ 4, $J_{H^a.H^b}$ 10 Hz, 1 H, H^b), 6.48 (d, $J_{H^a.H^b}$ 10 Hz, 1 H, H^a), 7.1—7.5 (m, 2 H, ArH) and 7.8—8.1 (m, 1 H, ArH); $\nu_{max.}$ (neat, mixture) 1 718 (imide), 1 664 (imide), 1 422, 1 366, 1 292, and 762 cm^{-1}. Because of the instability of the compounds, a satisfactory elemental analysis was not obtained. The stereoisomers could not be separated owing to this instability and similar behaviour upon chromatography.

Irradiation of (1) *and* 2,3-*dimethylbuta*-1,3-*diene* (9c). Irradiation gave a stereoisomeric mixture of 2,11-dimethyl-11-isopropenyl-2,3,3a,4-tetrahydro-3a,4-ethano-2-azaphenalene-1,3-diones (10c) as an oil; δ_H(CDCl$_3$) (major isomer) 1.27 (s, 3 H, CMe), 1.35 (s, 3 H, CMe), 2.02 (dd, 1 H, CH$_2$), 2.79 (dd, 1 H, CH$_2$), 3.26 (s, 3 H, NMe), 3.4—3.6 (m, 1 H, H^c), 4.54 (br s, 2 H, C=CH$_2$), 6.27 (dd, $J_{H^b.H^c}$ 5, $J_{H^a.H^b}$ 9 Hz, 1 H, H^b), 6.65 (d, $J_{H^a.H^b}$ 9 Hz, 1 H, H^a), 7.0—7.4 (m, 2 H, ArH), and 7.8—8.0 (m, 1 H, ArH); δ_H (minor isomer) 1.18 (s, 3 H, CMe), 1.35 (s, 3 H, CMe), 1.8—2.5 (m, 2 H, CH$_2$), 3.20 (s, 3 H, NMe), 3.4—3.6 (m, 1 H, H^c), 4.72 (br s, 2 H, C=CH$_2$), 3.20 (s, 3 H, NMe), 3.4—3.6 (m, 1 H, H^c), 4.72 (br s, 2 H, C=CH$_2$), 6.29 (dd, 1 H, H^b), 6.63 (d, 1 H, H^a), 7.0—7.4 (m, 2 H, Ar H), and 7.8—8.0 (m, 1 H, ArH); $\nu_{max.}$ (neat, mixture) 1 718 (imide), 1 670 (imide), 1 430, 1 370, 1 295, and 765 cm^{-1}. Because of the instability of the compound, a satisfactory elemental analysis was not obtained. The stereoisomers could not be separated owing to this instability and similar behaviour upon chromatography.

Irradiation of (1) *and* 2,5-*dimethylbuta*-2,4-*diene* (9d). Irradiation gave a stereoisomeric mixture of (E)-2-*methyl*-3-(3-*methylbut*-2-*enylidene*)-2,3-*dihydro*-2-*azaphenalen*-1-*one* (13a) and its (Z)-*isomer* (13b) as an oil; δ_H(CDCl$_3$) (13a) 1.80 (s, 6 H, CMe$_2$), 3.41 (s, 3 H, NMe), 6.14 (s, 2 H, H^a + H^b), 7.2—7.9 (m, 5 H, ArH), and 8.23 (d, 1 H, ArH); (13b) 1.80 (s, 6 H, CMe$_2$), 3.49 (s, 3 H, NMe), 6.06 (d, $J_{H^a.H^b}$ 11 Hz, 1 H, H^b), 6.10 (d, $J_{H^a.H^b}$ 11 Hz, 1 H, H^a), 7.2—7.9 (m, 5 H, ArH), and 8.36 (d, 1 H, ArH); $\nu_{max.}$ (neat) 1 642 (amide), 1 594, 1 370, and 776 cm^{-1} (Found: C, 82.4; H, 6.7; N, 5.0. C$_{18}$H$_{17}$NO requires C, 82.1; N, 6.5; N, 5.3%).

Irradiation of (1) *and furan* (14a). Irradiation gave (16a) and (17a). (E)-3-[3-*Formyloxy*-(Z)-*prop*-2-*enylidene*]-2-*methyl*-2,3-*dihydro*-2-*azaphenalen*-1-*one* (16a), m.p. 136—137 °C; δ_H(CDCl$_3$) 3.52 (s, 3 H, NMe), 6.14 (dd, $J_{H^b.R^1}$ 5.5, $J_{H^a.H^b}$ 11.3 Hz, 1 H, H^b), 6.39 (d, $J_{H^a.H^b}$ 11.3 Hz, 1 H, H^a), 7.32 (d, $J_{H^b.R^1}$ 5.5 Hz, 1 H, R^1), 7.4—8.1 (m, 5 H, ArH), 8.21 (s, 1 H, R^2), and 8.35 (d, 1 H, ArH); δ_C(CDCl$_3$) 31.1 (q, NMe), 104.4 (d, CH^a or CH^b),

110.9 (d, CH^a or CH^b), 125.5 (d), 126.4 (d), 127.3 (d), 127.5 (d), 128.2 (d), 131.7 (d, ArC), 134.1 (d, CR^1, deduced from the larger coupling constant than those of ArC), 138.5 (s, NC=CH^a), 156.8 (s, amide), and 160.3 (s, OCOR^2) (aromatic quaternary carbons were not observed); $\nu_{max.}$(KBr) 1 735 (ester), 1 665 (amide), 1 358, 1 308, 1 155, and 1 134 cm^{-1} (Found: C, 73.0; H, 4.5; N, 5.1. C$_{17}$H$_{13}$NO$_3$ requires C, 73.1; H, 4.7; N, 5.0%).

(Z)-3-[3-*Formyloxy*-(Z)-*prop*-2-*enylidene*]-2-*methyl*-2,3-*dihydro*-2-*azaphenalen*-1-*one* (17a), m.p. 90—93 °C; δ_H(CDCl$_3$) 3.58 (s, 3 H, NMe), 6.07 (dd, $J_{H^b.R^1}$ 5.8, $J_{H^a.H^b}$ 11.6 Hz, 1 H, H^b), 6.50 (d, $J_{H^a.H^b}$ 11.6 Hz, 1 H, H^a), 7.30 (d, $J_{H^b.R^1}$ 5.8 Hz, 1 H, R^1), 7.4—8.1 (m, 5 H, ArH), 8.21 (s, 1 H, R^2), and 8.33 (d, 1 H, ArH); $\nu_{max.}$(KBr) 1 738 (ester), 1 668 (amide), 1 362, 1 311, 1 152, and 1 130 cm^{-1} (Found: C, 73.2; H, 4.7; N, 5.1%).

Irradiation of (1) *and* 2,5-*dimethylfuran* (14b). Irradiation gave a stereoisomeric mixture of (E)-3-[3-*acetoxy*-3-*methyl*-(Z)-*prop*-2-*enylidene*]-2-*methyl*-2,3-*dihydro*-2-*azaphenalen*-1-*one* (16b) and its (Z)-*isomer* (17b), m.p. 45—50 °C; δ_H(CDCl$_3$) (16b) 2.00 (s, 3 H, R^2), 2.19 (s, 3 H, R^1), 3.40 (s, 3 H, NMe), 6.64 (s, 2 H, H^a + H^b), 7.1—8.0 (m, 5 H, ArH), and 8.27 (d, 1 H, ArH); (17b) 2.00 (s, 3 H, R^2), 2.19 (s, 3 H, R^1), 3.53 (s, 3 H, NMe), 5.94 (d, $J_{H^a.H^b}$ 11 Hz, 1 H, H^b), 6.08 (d, $J_{H^a.H^b}$ 11 Hz, 1 H, H^a), 7.1—8.0 (m, 5 H, ArH), and 8.20 (d, 1 H, ArH); $\nu_{max.}$(KBr) 1 758 (ester), 1 660 (amide), 1 598, 1 378, 1 218, and 1 163 cm^{-1} (Found: C, 74.0; H, 5.4; N, 4.55. C$_{19}$H$_{17}$NO$_3$ requires C, 74.25; H, 5.6; N, 4.6%).

References

1 P. H. Mazzocchi, in 'Organic Photochemistry,' ed. A. Padwa, Marcel Dekker, New York, 1981, vol. 5, p. 421; Y. Kanaoka, *Acc. Chem. Res.*, 1978, **11**, 407.
2 K. Maruyama and Y. Kubo, *J. Org. Chem.*, 1977, **42**, 3215.
3 K. Maruyama, T. Ogawa, and Y. Kubo, *Chem. Lett.*, 1978, 1107; Y. Kanaoka, K. Yoshida, and Y. Hatanaka, *J. Org. Chem.*, 1979, **44**, 664.
4 G. O. Schenck, W. Hartmann, S.-V. Mannsfeld, W. Metzner, and C. H. Krauch, *Ber.*, 1962, **95**, 1642.
5 H. D. Scharf and F. Korte, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 429; *Ber.*, 1965, **98**, 764, 3672; 1966, **99**, 1299.
6 (a) K. Maruyama, Y. Kubo, M. Machida, K. Oda, Y. Kanaoka, and K. Fukuyama, *J. Org. Chem.*, 1978, **43**, 2303; (b) K. Maruyama and Y. Kubo, *Chem. Lett.*, 1978, 851; (c) P. H. Mazzocchi, S. Minamikawa, and P. Wilson, *Tetrahedron Lett.*, 1978, 4361; (d) K. Maruyama and Y. Kubo, *J. Am. Chem. Soc.*, 1978, **100**, 7772; (e) M. Machida, K. Oda, K. Maruyama, Y. Kubo, and Y. Kanaoka, *Heterocycles*, 1980, **14**, 779; (f) P. H. Mazzocchi and F. Khachik, *Tetrahedron Lett.*, 1981, 4189; (g) K. Maruyama and Y. Kubo, *J. Org. Chem.*, 1981, **46**, 3612; (h) K. Maruyama and Y. Kubo, *J. Org. Chem.*, 1985, **51**, 1426.
7 P. H. Mazzocchi, M. Bowen, and N. Narian, *J. Am. Chem. Soc.*, 1977, **99**, 7063; P. H. Mazzocchi, S. Minamikawa, and M. Bowen, *J. Org. Chem.*, 1978, **43**, 3079; K. Maruyama and Y. Kubo, *Chem. Lett.*, 1978, 769; Y. Kanaoka, K. Yoshida, and Y. Hatanaka, *J. Org. Chem.*, 1979, **44**, 664; P. H. Mazzocchi, S. Minamikawa, P. Wilson, M. Bowen, and N. Narian, *ibid.*, 1981, **46**, 4864; P. H. Mazzocchi, P. Wilson, F. Khachik, L. Klingler, and S. Minamikawa, *ibid.*, 1983, **48**, 2981.
8 M. Machida, H. Takeuchi, and Y. Kanoaka, *Tetrahedron Lett.*, 1982, 4981; P. H. Mazzocchi, L. Klingler, M. Edwards, P. Wilson, and D. Shook, *ibid.*, 1983, 143; P. H. Mazzocchi and L. Klingler, *J. Am. Chem. Soc.*, 1984, **106**, 7567.

9 P. H. Mazzocchi, C. Somich, and C. Ammon, *Tetrahedron Lett.*, 1984, 3551.

10 Y. Kubo, S. Tojo, M. Suto, R. Toda, and T. Araki, *Chem. Lett.*, 1984, 2075.

11 J. J. McCullough, W. K. MacInnis, C. J. L. Look, and R. Faggiani, *J. Am. Chem. Soc.*, 1982, **104**, 4644.

12 G. Jones, II, in 'Organic Photochemistry,' ed. A. Padwa, Marcel Dekker, New York, 1981, vol, 5, p. 1.

13 L. M. Jackman and S. Sternhell, in 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, London, 1969, p. 302.

14 S. Toki, K. Shima, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 760; *ibid.*, 1966, **39**, 1806.

15 J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, 1972, **94**, 4040; M. P. Niemczyk, N. E. Schore, and N. J. Turro, *Mol. Photochem.*, 1973, **5**, 69; N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, 1975, **97**, 2482.

16 (a) A. Weller, *Pure Appl. Chem.*, 1968, **16**, 115; (b) H. Knibbe, D. Rehn, and A. Weller, *Z. Bunsenges, Physik. Chem.*, 1968, **72**, 257; (c) C. Pac, T. Sugioka, and G. Sakurai, *Chem. Lett.*, 1972, 39; (d) T. Sugioka, C. Pac, and H. Sakurai, *ibid.*, 1972, 667.

17 (a) E. J. Corey, J. D. Bars, R. LeMahierr, and R. B. Mirta. *J. Am. Chem. Soc.*, 1964, **86**, 5779; (b) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *ibid.*, 1973, **95**, 2549; (c) R. O. Loutfy and P. deMayo, *ibid.*, 1977, **99**, 3559.

18 (a) C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 238; (b) K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc.. Chem. Commun.*, 1974, 648; (c) K. Mizuno, C. Pac, and H. Sakurai, *J. Org. Chem.*, 1977, **42**, 3313; (d) R. A. Caldwell, N. T. Ghali, C.-K. Chien, D. DeMarco, and L. Smith, *J. Am. Chem. Soc.*, 1978, **100**, 2857; (e) R. A. Caldwell and T.-S. Maw, *J. Photochem.*, 1979, **11**, 165.

19 N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. R. Hautala, D. Morton, N. Niemczyk, and N. Schore, *Acc. Chem. Res.*, 1972, **5**, 92; D. Creed and R. A. Caldwell, *J. Am. Chem. Soc.*, 1974, **96**, 7369; J. D. Coyle, *Chem. Rev.*, 1978, **78**, 97.

20 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, Vol. 4, 2370.