学 位 申 請 論 文

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論 文 内 容 の 要 旨

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（論 文 題 目）

Photochemical Reactions of Epoxyquinones
（エポキシキノン類の光化学反応に関する研究）

（論文内容の要旨）

　エポキシキノン構造をもつ化合物はフレノリシン等の天然産化合物の中にも見出されるものであるが、その光化学反応については未だ殆んど未開拓の分野と云ってよい。申請者の論文は、エポキシキノンと種々の化合物との間の光化学反応について研究したものである。

　論文、その１）では、2,3－ジメチル－2,3－エポキシ－1,4－ナフトキノンをベンゼン中で各種のアルデヒドの共存下に光を照射すると、1,3－ジオキソラン付加体のエンド体とエキソ体の二つの立体異性体の混合物が生成することを見出している。脂肪族アルデヒドでは常にエンド体の方が多く生成し、その比率はアルキル基が大きくなるにつれて減少し、他方、芳香族アルデヒドでは、エキソ体が多量に生成することを見出している。これは付加の遷移状態に於いて π 電子軌道の重なりの効果よりも、単純に立体的反撥の効果の方が大きく作用することを示す事実である。さらに、

生成した付加体は、短波長の光によって光異性化反応を行い、アルキリデンフタリドーE、及びーZへ変化することを見出している。光異性化反応の量子収率を求め、開裂が生じる結合の方向性から、Norrish Type 1型の開裂から、この光異性化が進むことを推論している。また酸素とも光付加反応を行ないオゾニドが生成することを見出し、一重項酸素の関与する反応であることを指摘している。

　論文その2）では、エポキシキノンのカルボニル基から見てγ位に水素を持つ9種のエポキシナフトキノンについて、その分子内水素引抜き反応と、オキシラン環開裂との間の競争反応を行なわせ、この様な環境下にあっては、分子内水素引抜き反応が優先することを見出した。こうして水素引抜き反応に始まり、環化、異性化が起こり、ベンゾ〔3,3,0〕オクタジオン型の化合物が生成することを見出している。と同時にジヒドロベンゾフラン型の化合物も生成する。これは、2次的な転位反応の開始が光化学的なオキシラン環開裂によって始まり、生じたジラジカルのC－C転位、又はC－O転位に伴う安定化反応によって理解できることを示している。ついで消光実験を行ない、この2次的な光異性化反応が最低励起三重項から起こることを推定している。

　参考論文は大部分が本論文と関連したエポキシキノンの光化学反応と関連したものであって、申請論文の基礎となっている。

(1)   "Revised II"

Photochemistry of Epoxyquinone 5. Photoinduced Cycloadditions
of Epoxynaphthoquinone to Aldehydes, Ketones, and Oxygen[1,2]

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Abstract; Irradiation of a benzene solution of 2,3-dihydro-2,3-
dimethyl-2,3-epoxy-1,4-naphthoquinone (3a) in the presence of
aldehydes gives the primary 1,3-dioxolane adducts in good
yields. Upon further irradiation, the primary adducts undergo
photorearrangement to give alkylidene phthalides. A similar
photocycloaddition reaction of 3a with aliphatic ketones was
realized by the use as the reaction medium. When irradiated
in the presence of oxygen in benzene, 3a was converted into
3-acetyl-3-acetoxyphthalide and 3-acetoxy-3-methylisochroman-
1,4-dione presumably *via* the reaction of singlet oxygen with
a carbonyl ylide 4a. In contrast to 2,3-dialkyl epoxynaphtho-
quinones 3a-d, the photoinduced cycloaddition of 2,3-dihydro-
2,3-diphenyl-1,4-naphthoquinone (3e) to carbonyl compounds
did not occur. The photoinduced cycloadditions of epoxynaphtho-
quinones to carbonyl compounds are believed to be HOMO-controlled
reactions on the basis of substituent effects at 2- and 3-positions
of epoxynaphthoquinones and at *para*-position of the dipolarophiles,
namely aromatic aldehydes.

Ring-opening reactions at C-C bonds of oxiranes have attracted considerable interest from both synthetic and mechanistic stand-points.[3,4] Especially, 1,3-dipolar cycloaddition of carbonyl ylides to carbonyl compounds constitues among the most convenient methods for the synthesis of 1,3-dioxolane compounds. While several examples of 1,3-dipolar cycloaddition reactions of thermally generated carbonyl ylides with less volatile carbonyl compounds can be found in literature,[5] relatively little is known about the cycloaddition of photogenerated carbonyl ylides to carbonyl compounds. In one system, Pete *et al.* have recently described the photocycloaddition reaction of the α,β-epoxy ketone 1 to acetone leading to the formation of the 1,3-dioxolane 2.[6] Recently, we have reported that irradiation of several epoxynaphthoquinones give carbonyl ylides 4 or 1,3-diradical 5, which may be trapped by alkenes or dipolarophiles such as 2-norbornene and N-phenylmaleimide.[7] When irradiated in a benzene solution (0.1 M) in the absence of 1,3-dipolarophile, 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (3a) is converted into dimers 6a and 6b in good yields *via* the cycloaddition of 4a or 5a to the carbonyl group of another molecule of 3a.[1] This result prompted to investigate the possibility of trapping of 4 or 5 with simple aldehydes and ketones. In this paper, the photolyses of epoxynaphthoquinones in the presence of various aldehydes and ketones were examined and the 1,3-dipolar cycloadditions of 4 or 5 to aldehydes and ketones as well as the photoinduced oxygenation of 3a are reported.

Results and Discussion

Photoinduced Cycloaddition of 3a to Aldehydes

Irradiation of a benzene solution of 3a (0.012 $\underline{M}$) in the presence of acetaldehyde 7a (0.15 $\underline{M}$) with radiation of wavelength above 300 nm for 30 min afforded a 1.7:1 mixture of 1,3-dioxolanes 8a and 9a in high yield (92% by ^{1}H-NMR). The products were separated by silica gel chromatography; 8a (49%) and 9a (22%), and characterized by their spectral data and elemental analyses (see experimental section). Similar reactions with aliphatic aldehydes 7b-7h and aromatic aldehydes 7i-7m gave 1,3-dioxolanes 8 and 9 in moderate to high yields and the results are summarized in Table I and II. The b-methyl protons of 9i-9m are characterized by a marked upfield shift (δ 1.12-1.14) resulting from shielding by the aromatic ring. In the ^{1}H-NMR spectra of 9i-9m, the chemical shifts observed for H^c protons were lower relative to those of 8i-8m without exception, probably due to the proximity of carbonyl group to the H^c proton. On the basis of these observations, 8a-8g and 9a-9g were assigned to be *endo* and *exo* structures, respectively, by the comparison of of the chemical shifts of H^c methine protons. Consistent with this assignment is the fact that b-methyl protons of 9a-9e were slightly shielded by the steric repulsion by the *vicinal* alkyl groups compared with those of 8a-8e. Further, the H^d protons of 8d are considerably shielded at δ 1.50 by the aromatic
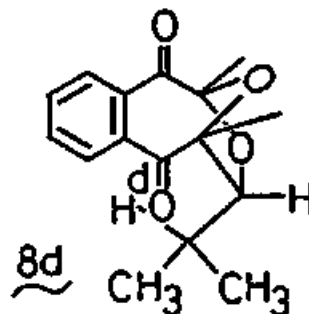
rings, presumably because of restricted rotation of the iso-propyl group (compare H^d of 9d at δ 1.96). The ratios of 8 to 9 (*endo/exo*) formed in the reaction were readily determined by high-performance LC (HPLC) and are listed in Table I. In the case of aliphatic aldehydes, *endo* adducts 8 were formed preferentially, while *exo* adducts 9 were the predominant products in the reaction with aromatic aldehydes. It seems likely that *endo* approach is more hindered, since *endo/exo* ratios decreased with increasing bulkiness of alkyl group of aliphatic aldehydes from 7a to 7e. Therefore, preferential formation of *endo* adducts 8 in the reaction with aliphatic aldehydes implies two points that electronic interactions between the 1,3-dipole and alkyl groups of aliphatic aldehydes must be operative in the transition state and that the cycloaddition with aliphatic aldehydes appears to proceed in a concerted fashion,[8] for if intermediate 10 or 11 intervened, free rotation around the C-O bond would be expected to take place prior to ring closure, probably resulting in the preferential formation of less hindered *exo* adducts 9. On the other hand, preferential formation of *exo* adducts in the reaction with aromatic aldehydes may be ascribed to either critical steric encumbrance by buttressing phenyl groups or a stepwise mechanism in which the intermediate 10 would be better stabilized by the aromatic rings.[5] Kobuke and Fueno have reported that a methyl group shows a greater tendency toward *endo*-orientation in Diels-Alder reaction with cyclopentadiene than most of electron-accepting polar groups, such as -CHO, -CN, and -COOH.[9] Intermolecular dispersion forces

were advanced to explain the origin of the *endo*-orientating ability of a methyl substituent, but a definitive explanation remains to be presented. It is reasonable to assume that electronic interactions between 4a or 5a and the alkyl groups of aliphatic aldehydes are similar in magnitude. The interplay of steric factors and ill-defined electronic factors would determine the *endo/exo* ratio.

The relative rates for the reaction of carbonyl ylide 4a or 1,3-diradical 5a with *para*-substituted benzaldehydes 7i-m were determined by using butyraldehyde 7c as a probe. A benzene solution of 3a, 7c, and aromatic aldehyde was irradiated for a short time that the relative ratio of two aldehydes did not change significantly from the initial ratio. Product yields were determined by HPLC.[10] The results in Table III show clearly that aromatic aldehydes are more reactive than butyraldehyde 7c and that electron-attracting substituents in the *para*-position of aromatic aldehydes accelerate the reaction.[11]

The primary 1,3-dioxolane adducts 8 and 9 proved photolabile and upon prolonged irradiation gave a mixture of alkylidene phthalides 12 and 13 in high yields.[2b]

Photoinduced Cycloaddition of 3a to Ketones

Solutions of 3a in the neat ketones were employed in the photochemical studies of aliphatic series, since such ketones are much less reactive toward 4a or 5a than the carbonyl group of 3a. Irradiation of an acetone solution of 3a (82.5 mM) gave the 1,3-dioxolane adduct 14a in 23% yield, in addition to dimers 6a (26%) and 6b (13%), indicating that acetone is only 3.6×10^{-3}

times as reactive as 3a. When irradiated in a dilute acetone
solution, 3a was converted to 14a in 85% yield. Similar 1,3-
dioxolanes 14b-d were obtained upon irradiation of 3a in solution
in various other ketones (Table IV). In these photolyses,
radiation of wavelength below 341 nm was almost absorbed by
ketones used as the solvent. It seems likely that for the most
part the excited ketones transfer energy to 3a, but also undergo
photochemical reactions such as α-cleavage which leads to products
which contaminate the reaction mixture (run 3 and 4 in Table IV).
In fact, 14b was obtained in a higher yield (53%) when the
irradiation was conducted with radiation filtered through an
acetone solution.

On the other hand, acetophenone 15 was found to be more
reactive toward 4a or 5a to the extent that irradiation of a
benzene solution of 3a (82.5 mM) and 15 (138 mM) gave the 1,3-
dioxolane 14e in 26% yield and the dimers 6a and 6b in 40 and 25%
yields, respectively. The ^{1}H NMR spectrum of 14e displays three
methyl singlets at δ 1.08, 1.48, and 1.86 ppm, which indicates
that configuration of the phenyl group in 14e is *exo*. Predominant
formation of the *exo*-phenyl adduct 14e may be ascribed to the
conjunction of *endo*-selectivity of the methyl substituent acting
in concert with the steric bulkiness of the phenyl group.
It is of interest to compare the relative reactivity of ketones
toward 4a or 5a by using the dimerization of 3a as a probe.
The results observed are listed in Table IV. Aromatic ketones 3a
and 15 react 10^2 times faster than aliphatic ketones and
curiously cyclohexanone is 10 times as reactive as acetone,

3-pentanone, and cyclopentanone.

Photoinduced Oxygenation of 3a

A dilute benzene solution of 3a (4 mM) was saturated with oxygen and irradiated through a Pyrex filter for 30 min while a stream of oxygen was passed through the solution. 3-Acetyl-3-acetoxyphthalide 16 (43%) and 3-acetoxy-3-methylisochroman-1,4-dione 17 (13%) were isolated as major products upon chromatographing the products on a Florisil column.[2c] Irradiation of a degassed benzene solution of 3a under similar conditions gave no products identified as 16 and 17. The effects of Rose Bengal and β-carotene suggest that siglet oxygen is involved in the photo-oxygenation of 3a.[2c] A tentative mechanism for the reaction is shown in Scheme II. Singlet oxygen adds to the carbonyl ylide 4a or 1,3-diradical 5a in a manner analogous to that observed for reactive dipolarophiles. The ozonide 18 thus formed undergoes a Baeyer-Villiger-type rearrangement to give the diketoanhydride 19 which finally undergoes isomerization to 16 and 17. Criegee et al. have found that closely related ozonides 20, which is known as one of the extremely stable ozonides, decomposes slowly to give 3-benzoyloxy-3-phenylphthalide 21.[13] Ullman and Henderson have reported that 20 readily undergoes photorearrangement to 22, and finally gives the isomerized product 21.

In recent years, reports have appeared in the literature that singlet oxygen will behave as a dipolarophile toward ylides,[15] diazoalkanes,[16] and nitrones,[17] however, the oxygenation of carbonyl ylides has been limited to stable pyrylium oxides such as the diphenylbenzopyrylium oxide 23[14] and 2,4,6-triphenyl-

pyrylium oxide 24.[18] It is of interest to note that this photo-
oxygenation proceeds *via* a photochemically generated transient
carbonyl ylide.

Effects of Substituents at 2,3-Positions of Epoxynaphtho-quinones.

The effect of substituents at 2,3-positions of epoxy-
naphthoquinones was investigated by irradiating epoxynaphthoquinones,
3b, 3c, 3d, and 3e in the presence of aldehydes and ketones.
Irradiation of a benzene solution of 3b (0.01 M) in the presence
acetaldehyde (0.2 M) for 1 h gave 1,3-dioxolane 25 (32%) and
26 (24%), together with 2-ethyl-3-hydroxy-1,4-naphthoquinone 27
(4%). The latter product suggests that a Norrish type II photo-
process has accompoanied the generation of 4b or 5b.[19] Irradi-
ation of a benzene solution of 3c and acetaldehyde gave four
1,3-dioxolanes, 28 (12%), 29 (9%), 30 (26%), and 31 (10%).

Irradiation of an acetone solution of 3b (0.01 M), however,
produced a complex mixture from which a low yield (7%) of 1,3-
dioxolane 32 was isolated, in addition to 27 (3%). Competitive
Norrish type II photoreaction of 3b and the low reactivity of
acetone as a dipolarophile for carbonyl ylides or 1,3-diradicals
might be responsible for the poor yield of 32. When irradiated
in acetone, epoxynaphthoquinone 3c, which has no γ-hydrogen atom,
was clearly converted into two 1,3-dioxolanes 33 (39%) and 34
(41%). Similarly, irradiation of an acetone solution of 3d
gave the corresponding 1,3-dioxolanes 35 (23%) and 36 (12%).

In contrast to 2,3-dialkyl substituted epoxynaphthoquinones,

no 1,3-dioxolanes are formed when 2,3-diphenyl-2,3-dihydro-2,3-
epoxy-1,4-naphthoquinone (3e) is irradiated in acetone or in the
presence of acetaldehyde (0.2 M) in benzene. Irradiation of a
benzene-methanol (40:1) solution of 3e containing Rose Bengal
and continuously saturated with oxygen affords no oxygenated
products. In all cases, only a slow photoisomerization to
alkylidene phthalides 37 and 38 takes place.[20] Therefore, the
carbonyl ylide 4e or 1,3-diradical 5e derived from 3e does not
react with electron-deficient 1,3-dipolarophiles such as aldehydes,
ketones, and singlet oxygen, in contrast to alkenes such as
2-norbornene and N-phenylmaleimide, where clean cycloaddition
reactions are observed.[7]

Recently, Houk *et al.* have suggested that the frontier
orbital energies of 1,3-dipoles are dominant factors in the
reactivities toward various dipolarophiles.[4a,b] Based on the
estimated frontier orbital energies, the parent carbonyl ylide
39 should be a typical HOMO-controlled dipole (the interaction
of the dipole HOMO with the dipolarophile LUMO is greatest),[4a]
but the tetracyano compound 40 has considerably lowered frontier
orbital energies and reacts most readily with electron-rich
dipolarophiles[3a] (LUMO-controlled dipole; the interaction of the
dipole LUMO with the dipolarophile HOMO is greatest). The less
electron-deficient carbonyl ylide 41 formed from 2,3-dicyano-
2,3-diphenyl oxirane is reactive with both electron-deficient
and electron-rich dipolarophiles (HOMO, LUMO-controlled dipole).[21]

It seems likely that carbonyl ylides 4a-d or 1,3-diradicals

__5a-d__ generated from 2,3-dialkyl substituted epoxynaphthoquinones
are best classified as HOMO, LUMO-controlled dipoles, since __4a-d__
or __5a-d__ react with both electron-deficient and electron-rich
dipolarophiles. On the other hand, HOMO orbiral of diphenyl
compound __4e__ or __5e__ appears to have much lower energy and fails to
interact significantly with the LUMO orbital of carbonyl
compounds. In the present cycloaddition reaction of __4a__ or __5a__
with carbonyl compounds, electron attracting substituents at the
para-positions of aromatic aldehydes accelerate the rate of
cycloaddition and aromatic carbonyl compounds are more reactive
than the corresponding aliphatic carbonyl compounds; _e.g.,_
benzaldehyde reacts 30-40 times faster than acetaldehyde and
acetophenone reacts 60-70 times faster than acetone. These
results indicate that the cycloaddition reaction of __4a__ or __5a__
with carbonyl compounds are HOMO-controlled.

In summary, irradiation of 2,3-dialkyl substituted epoxy-
naphthoquinones in the presence of aldehydes or ketones
leads to the formation of a new class of tricyclic 1,3-dioxolanes,
which, in turn, can be transformed into alkylidene phthalides in
good yields. The cycloaddition of the carbonyl ylide __4__ or
1,3-diradical __5__ to aldehydes or ketones may be designated as a
HOMO-controlled reaction, but the reaction fails to occur in the
case of the diphenyl substituted analog __4e__ or __5e__.

Experimental Section

General Methods. The instruments and procedures were as previuosly reported.[1]

Epoxynaphthoquinones 3a, 3b, and 3e were prepared by the method of Arakawa[7] and 3c and 3d prepared by epoxidation of the corresponding 1,4-naphthoquinones with NaOCl/pyridine. The 1,4-naphthoquinones were synthesized by the method of Jacobsen.[22]

2-Methyl-3-(2,2-dimethyl)propyl-1,4-naphthoquinone 42; mp 93-94.5°C; IR(KBr) 2910. 1660, 1600, and 1300 cm^{-1}; ^{1}H NMR (CDCl$_3$) 0.95(s, 9H), 2.22(s, 3H), 2.71(s, 2H), 7.6-7.7(m, 2H), and 8.1-8.2(m, 2H). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%. Found: C, 79.22; H, 7.53%.

2,3-Dihydro-2,3-epoxy-2-methyl-3-(2,2-dimethyl)propyl-1,4-naphthoquinone 3c; mp 113-115°C; IR(KBr) 2910, 1695, 1600, 1310, 720, and 710 cm^{-1}; ^{1}H NMR(CDCl$_3$) 1.02(s, 9H), 1.73(s, 3H), 1.72 and 2.70(ABq, J=14Hz, 2H), 7.2-7.6(m, 2H), and 7.6-7.8(m, 2H). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02%. Found: C, 74.52; H, 7.00%.

2-Methyl-3-(2-methyl-2-phenyl)propyl-1,4-naphthoquinone 43; mp 77-78°C; IR(KBr) 2920, 1665, 1655, 1595, 1295, 730, and 700 cm^{-1}; ^{1}H NMR(CDCl$_3$) 1.36(s, 6H), 1.67(s, 3H), 3.00(s, 2H), 7.2-7.4(m, 5H), 7.6-7.7(m, 2H), and 7.9-8.1(m, 2H). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%. Found: C, 82.45; H, 6.71%.

2,3-Dihydro-2,3-epoxy-2-methyl-3-(2-mehtyl-2-phenyl)propyl-1,4-naphthoquinone 3d; mp 113-114.5°C; IR(KBr) 2950, 1700, 1690, 1600, 1500, 1310, 1290, 940, and 720 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.43

(s, 3H), 1.46(s, 3H), 1.48(s, 3H), 2.13 and 2.93(ABq, J=14Hz,

2H), 7.2-7.6(m, 5H), 7.6-7.8(m, 2H), and 7.8-8.0(m, 2H). Anal.

Clacd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29%. Found: C, 78.66; H, 6.32%.

General Procedure for the Photochemical Reactions of

Epoxynaphthoquinones 3 with Aldehydes.   A solution of 3 (1 g)

and aldehyde (10 equiv to 3 in the case of aliphatic aldehydes,

and 5 equiv to 3 in the case of aromatic ones) in 500 mL of benzene

in a Pyrex vessel was bubbled with N_2 for 10 min and then

irradiated under cooling with water. The progress of the reaction

was followed by GC or HPLC. After 3 had been completely consumed,

irradiation was ceased. In the reactions with aliphatic aldehydes,

the solvent and excess aldehydes were removed under reduced

pressure and the resulting oil was chromatographed over silica

gel column using 5% ether/hexane as the eluant. The first com-

ponent was *endo* adduct 8 and the second was *exo* adduct 9. In the

reactions with aromatic aldehydes, after the solvent was removed

under reduced pressure, the resulting mixture was treated with

$KMnO_4$ solution in acetone-water (1:1) overnight at room temperature.

Then, the mixture was extracted with chloroform, and the organic

layer was washed successively with $NaHSO_3$ and $NaHCO_3$, and dried

(Na_2SO_4). The products were separated by chromatography on silica

gel column using 5% ether/hexane as the eluant. *exo* Adduct 9 eluted

first, then followed *endo* adduct 8. Yields and physical properties

of 8 and 9 were summarized in Table I, II, and V. Selected ^{13}C NMR data

are follows; 8a (CDCl$_3$) 202.2(C=O), 195.1(C=O), 134.3(s), 133.4(d),

133.2(d), 131.3(s), 130.6(d), 130.2(d), 106.8(s), 90.5(s), 80.8(d),

20.8(q), 20.0(q), and 14.5(q). 9a (CDCl$_3$) 205.8(C=O), 198.0(C=O),

134.1(s), 133.3(d), 133.2(d), 132.4(s), 129.7(d), 129.3(d), 107.3
(s), 89.9(s), 78.5(d), 22.3(q), 17.7(q), and 17.0(q).

General Procedure for the Photochemical Reaction of 3

with Ketones.   Typically, that for the reaction of 3a with

acetone was described. A solution of 3a (1 g) in 600 mL of acetone

was irradiated for 30 min. After removal of the solvent *in vacuo*,

the resulting semisolid material was trituated with hexane ,

giving colorless crystals of 14a (1.09 g, 85%).

Detailed reaction conditions, product yields, and physical

properties were summarized in Table VI and V. ^{13}C NMR (CDCl$_3$) data of

14a; 203.3(C=O), 196.3(C=O), 134.2(s), 133.6(d), 133.2(d), 131.4
(s), 130.5(d), 130.3(d), 106.2(s), 92.4(s), 83.9(s), 25.4(q),
24.1(q), 22.2(q), and 19.4(q).

Photoinduced Oxygenation of 3a in Benzene.   A solution

of 3a (500 mg) in 600 mL of benzene was bubbled with O$_2$ for 30 min

at room temperature and then irradiated for 30 min under a slow

stream of O$_2$ bubbling. The solvent was removed *in vacuo* to

leave a yellow oil, which was separated on a Florisil Column using

ether/hexane as the eluant, giving 3-acetyl-3-acetoxyphthalide

16 (249 mg, 43%) and 3-acetoxy-3-methylisochroman-1,4-dione 17

(75 mg, 13%).[2c]

16; mp 97-99°C; Anal. Calcd for C$_{12}$H$_{10}$O$_5$: C, 61.54; H, 4.30%.
Found: C, 61.23; H, 4.65%. Mass m/e 218(M[+]-18, 1) 192(30), 191(20),
176(5), 175(7), and 148(100).

17; mp 101-102°C; Anal. Calcd for C$_{12}$H$_{10}$O$_5$: C, 61.54; H, 4.30%.
Found: C, 61.28; H, 4.71%. Mass m/e 218(M[+]-18, 3), 191(25), and
148(100).

To a benzene solution of <u>3a</u> (500 mg, in 600 mL) was added a solution of Rose Bengal (30 mg) in 10 mL of methanol. The solution was bubbled with O_2 for 30 min and then irradiated for 30 min under a slow stream of O_2 bubbling. Separation of the products on a Florisil column gave <u>16</u> (394 mg, 68%) and <u>17</u> (93 mg, 16%).

A solution of <u>3a</u> (500 mg) and β-carotene (30 mg) in 600 mL of benzene was similarly irradiated for 1 h. The starting epoxynaphthoquinone <u>3a</u> was recovered (260 mg), and products were the dimers, <u>6a</u>(60 mg, 25%) and <u>6b</u>(20 mg, 8.3%).

References and Notes

1) Part 4, Maruyama, K; Osuka, A. J. Org. Chem. 1980, 45, 1898.

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(11)
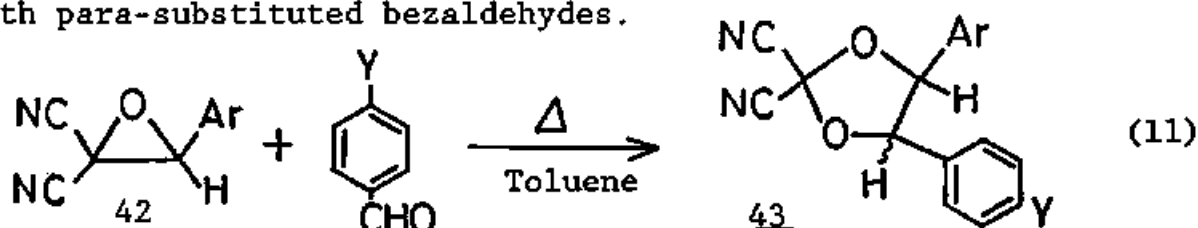
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Table I.   Photo-induced Cycloaddition of 3a to Aldehydes

Aldehyde	R	Total yields[a]	8/9[b]	Products	(mp °C)
7a	Me	71 (91)[c]	1.7	8a (98)	9a (75-76.5)
7b	Et	75	1.9	8b (92-93)	9b (80-81)
7c	Pr	65	1.8	8c (oil)	9c (82-84)
7d	i-Pr	60	1.0	8d (94)	9d (90-91)
7e	$(Et)_2CH$	70	1.2	8e (96-97)	9e (85-87)
7f	$PhCH_2$	59	2.0	8f (125-126)	9f (141-142)
7g	Ph_2CH	46	1.4	8g (121-122)	9g (167-168)
7h	$CH_3(CH_2)_{10}$	29	d	8h (100-101)	-
7i	$p-NO_2-Ph$	86	0.33	8i (165-166)	9i (187)
7j	p-MeO-Ph	70	0.23	8j (148-149)	9j (152-153)
7k	p-Me-Ph	76	0.37	8k (130-131)	9k (158-159)
7l	Ph	82	0.35	8l (132-133)	9l (146-147)
7m	p-Cl-Ph	80	0.65	8m (168-170)	9m (175-176)

a, Isolated yields. b, Product ratios 8/9 were determined by HPLC.

c, ^{1}H-NMR yield. d, Not determined.

Table II. ^{1}H-NMR Data of Primary Adducts 8 and 9

Compound	H^a	H^b	H^c	Compound	H^a	H^b	H^c
8a	1.66	1.56	4.00(q)	9a	1.66	1.48	4.32(q)
8b	1.66	1.56	3.72(dd)	9b	1.66	1.48	4.00(dd)
8c	1.65	1.56	3.85(dd)	9c	1.65	1.48	4.10(dd)
8d	1.64	1.60	3.48(d)	9d	1.64	1.55	3.62(d)
8e	1.64	1.62	3.78(d)	9e	1.62	1.53	3.96(d)
8f	1.70	1.58	4.18(dd)	9f	1.82	1.62	4.50(dd)
8g	1.76	1.19	4.82(d)	9g	1.70	1.24	5.24(d)
8h	1.62	1.52	4.10(dd)				
8i	1.87	1.80	5.08(s)	9i	1.92	1.14	5.28(s)
8j	1.85	1.74	5.00(s)	9j	1.88	1.14	5.16(s)
8k	1.83	1.70	5.08(s)	9k	1.88	1.12	5.20(s)
8l	1.84	1.72	5.06(s)	9l	1.89	1.12	5.20(s)
8m	1.84	1.72	5.03(s)	9m	1.89	1.14	5.22(s)

a, As to the data of H^d, see Table V.

Table III.   Relative Rates of para-Substituted

Benzaldehydes toward $\underline{3a}$

Aldehyde	Substituent	Relative Rate
$\underline{7i}$	$-NO_2$	103
$\underline{7m}$	$-Cl$	44
$\underline{7l}$	$-H$	30
$\underline{7k}$	$-CH_3$	17
$\underline{7j}$	$-MeO$	4.0
$\underline{7c}$	$-$	1

Table VI. Photo-induced Cycloaddition of 3a to Ketones

Run	Ketone	Conc. (mM)[a]	Irradiation Time (h)	Product Distribution[b] (%) 14(mp,°C)	Dimers[c]	Relative Reactivity to 3a (x 10^3)
1	acetone	82.5	12	14a(86.5-87) ; 23	39	3.6
2	acetone	8.25	1	14a ; 85	-	-
3	2-pentanone	40	1.5	14b(55-57); 12	12	4.2
4	2-pentanone	10	1	14b ; 17	-	-
5	2-pentanone	10	22[d]	14b ; 53	-	-
6	cyclopentanone	82.5	12	14c(58-59) ; 19	51	2.7
7	cyclopentanone	8.25	1	14c ; 69	18	2.8
8	cyclohexanone	82.5	12	14d(85) ; 57	21	23
9	cyclohexanone	8.25	1	14d ; 78	-	-
10	acetophenone[e]	82.5	2.5	14e(123-125) ; 26	65	240

a, Concentration of 3a. b, Isolated yields based on the consumed amount of 3a. c, Sum of the yields of dimers, 6a + 6b. d, Irradiation was carried out through an acetone filter. e, A benzene solution of acetophenone (133 mM) was irradiated.
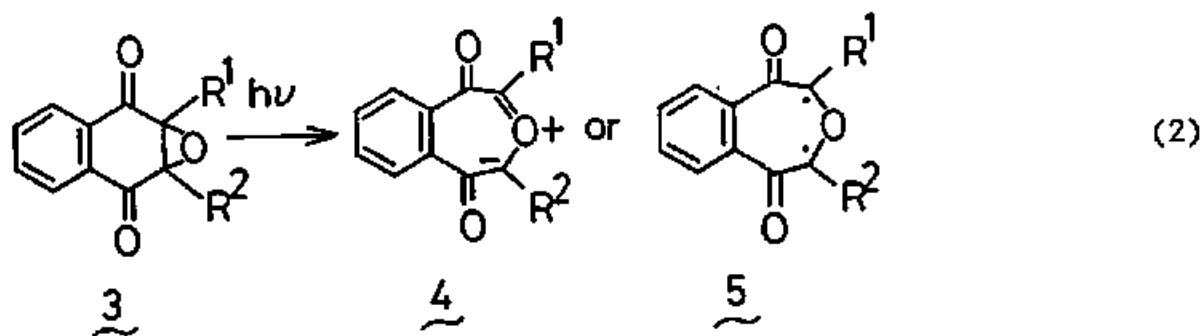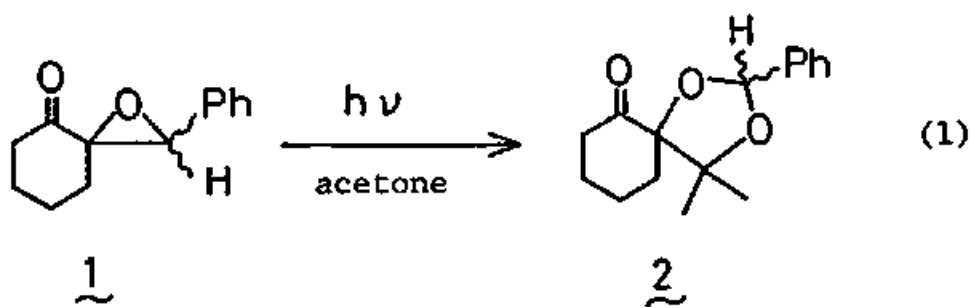
Compound	Formula	Elemental Analysis Calcd(%)	Found(%)	IR(KBr) $\nu_{max}(cm^{-1})$	^1H NMR(CDCl$_3$) δ(ppm)
<u>8e</u>	$C_{18}H_{22}O_4$	C, 70.81 H, 6.99	70.94 6.87	1680, 1600, 1160	0.77(t, J=6, 3H), 0.89(t, J=6, 3H), 1.2-1.6(m, 5H), 7.6-8.2(m, 4H)
<u>9e</u>	$C_{18}H_{22}O_4$	C, 70.81 H, 6.99	70.97 7.03	1690, 1595, 1155	0.90(t, J=6, 3H), 0.94(t, J=6, 3H), 1.2-1.7(m, 5H), 7.7-8.2(m, 4H)
<u>8f</u>	$C_{20}H_{18}O_4$	C, 74.52 H, 5.63	74.76 5.68	1705, 1680, 1595 1170	2.62(dd, J=4,16, 1H), 2.96(dd, J=8,16, 1H), 7.2(m, 5H), 7.6-7.8(m, 2H), 8.0-8.2(m, 1H)
<u>9f</u>	$C_{20}H_{18}O_4$	C, 74.52 H, 5.63	74.36 5.90	1690, 1590, 1165	2.9(m, 1H), 2.98(m, 1H), 7.2(m, 5H), 7.6-8.0(m, 4H)
<u>8g</u>	$C_{26}H_{22}O_4$	C, 78.37 H, 5.57	78.40 5.52	1700, 1680, 1600 1180	3.96(d, J=10, 1H), 7.0-7.4(m, 10H), 7.6-7.8(m, 2H), 7.9-8.2(m, 2H)
<u>9g</u>	$C_{26}H_{22}O_4$	C, 78.37 H, 5.57	78.45 5.62	1705, 1685, 1595 1290	4.20(d, J=10,1H), 7.1-7.5(m, 10H), 7.6-8.0(m, 4H)
<u>8h</u>	$C_{24}H_{34}O_4$	C, 74.57 H, 8.87	74.27 9.15	2950, 1690, 1580 1160	0.88(t, J=6, 3H), 1.0-1.5(m, 20H), 7.6-8.1(m, 4H)
<u>8j</u>	$C_{20}H_{18}O_5$	C, 70.99 H, 5.36	70.55 5.52	1680, 1600, 1360,	3.70(-OC$\underline{H}_3$), 6.70(d, J=7, 2H), 6.96(d, J=7, 2H), 7.9-8.3(m, 4H)
<u>9j</u>	$C_{20}H_{18}O_5$	C, 70.99 H, 5.36	71.03 5.34	1685, 1590, 1340	3.76(-OC$\underline{H}_3$), 6.86(d, J=7, 2H), 7.24(d, J=7, 2H), 7.6-8.0(m, 4H)
<u>8k</u>	$C_{20}H_{18}O_4$	C, 74.52 H, 5.63	74.77 5.92	1680, 1595, 1350,	2.26(s, 3H), 6.92(d, J=7, 2H), 7.9-8.3(m, 4H),
<u>9k</u>	$C_{20}H_{18}O_4$	C, 74.52 H, 5.63	74.77 5.66	1685, 1600, 1370	2.34(s, 3H), 7.16(m, 4H), 7.6-8.0(m, 4H)
<u>8l</u>	$C_{19}H_{16}O_4$	C, 74.01 H, 5.23	74.33 5.51	1680, 1590, 1350	7.2(m, 5H), 7.9-8.2(m, 4H)
<u>9l</u>	$C_{19}H_{16}O_4$	C, 74.01 H, 5.23	74.22 5.33	1690, 1598, 1350	6.94(d, J=6, 2H), 7.16(d, J=6, 2H), 7.9-8.2(m, 4H)

Compound	Formula	Elemental Analysis Calcd(%)	Found(%)	IR(KBr) $\nu_{max}(cm^{-1})$	^{1}H NMR(CDCl$_3$) δ(ppm)
8m	$C_{19}H_{15}ClO_4$	C, 66.58	66.41	1680, 1600, 1350	6.94(d, J=6, 2H), 7.16(d, J=6, 2H), 7.9-8.2
		H, 4.41	4.37		(m, 4H)
		Cl, 10.34	10.22		
9m	$C_{19}H_{15}ClO_4$	C, 66.58	66.83	1685, 1595, 1340	7.26(d, J=6, 2H), 7.32(d, J=6, 2H), 7.6-8.0
		H, 4.41	4.22		(m, 4H)
		Cl, 10.34	10.30		
14a	$C_{15}H_{16}O_4$	C, 69.21	69.20	2990, 1680, 1590	1.18(s, 3H), 1.40(s, 3H), 1.50(s, 3H), 1.70
		H, 6.20	6.27	1150	(s, 3H), 7.6-7.8(m, 2H),8.0-8.2(m, 2H)
14b	$C_{17}H_{20}O_4$	C, 70.81	70.77	2990, 1685, 1595	0.84(t, J=7, 3H), 1.00(t, J=7, 3H), 1.53(s, 3H),
		H, 6.99	6.85	1460, 1275, 1170	1.67(s, 3H), 1.26(q, J=7, 2H), 1.76(q, J=7, 2H),
					7.5-7.7(m, 2H), 7.9-8.0(m, 2H)
14c	$C_{17}H_{18}O_4$	C, 71.31	71.42	2980, 1690, 1595	1.52(s, 3H), 1.68(s, 3H), 1.2-1.9(m, 8H),
		H, 6.34	6.29	1375, 1275, 1160	7.6-7.8(m, 2H), 7.9-8.2(m, 2H)
14d	$C_{18}H_{20}O_4$	C, 71.98	72.00	2930, 1680, 1590	1.48(s, 3H), 1.69(s, 3H), 1.0-2.0(m, 10H),
		H, 6.71	6.75	1445, 1375, 1270	7.6-7.8(m, 2H), 8.0-8.2(m, 2H)
14e	$C_{20}H_{18}O_4$	C, 74.52	74.59	2990, 1680, 1600	7.2-7.5(m, 5H), 7.6-7.7(m, 2H), 7.8-8.0(m, 2H)
		H, 5.63	5.65	1250	
25	$C_{16}H_{18}O_4$	C, 70.05	70.02	2990, 1690, 1600	0.93(t, J=6, 3H), 1.03(t, J=7, 3H), 1.22(d, J=7,3H),
		H, 6.61	6.72	1150	1.6-2.4(m, 4H), 4.08(q, J=7, 1H), 7.6-8.1(m, 4H)
26	$C_{16}H_{18}O_4$	C, 70.05	70.11	2990, 1695, 1600	0.93(t, J=6, 3H), 0.96(t, J=6, 3H), 1.30(d, J=7, 3H),
		H, 6.61	6.62	1150	1.6-2.4(m, 4H), 4.33(q, J=7, 3H), 7.7-8.0(m, 4H)
28	$C_{18}H_{22}O_4$	C, 71.50	71.72	2990, 1695, 1590	0.92(s, 9H), 1.20(d, J=6, 3H), 1.73(s, 3H), 1.73
		H, 7.33	7.19	1140	and 2.22(ABq, J=14, 2H), 4.00(q, J=6, 1H),
					7.6-8.0(m, 4H)

Table V. (Continued)

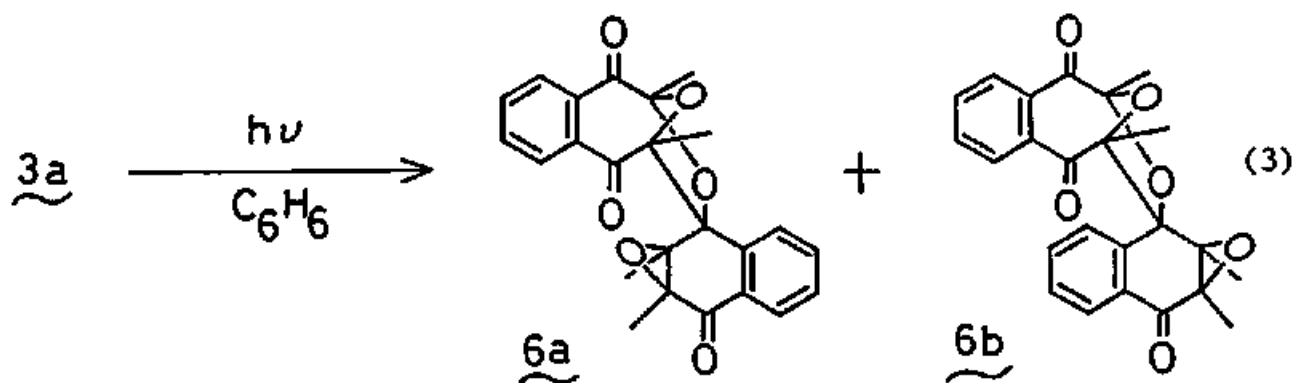| Compound	Formula	Elemental Analysis Calcd(%)	Found(%)	IR(KBr) $\nu_{max}(cm^{-1})$	^1H NMR($CDCl_3$) δ(ppm)
29	$C_{18}H_{22}O_4$	C, 71.50 H, 7.33	71.52 7.53	2990, 1680, 1600 1150	0.91(s, 9H), 1.27(d, J=7, 3H), 1.70(s, 3H), 1.63 and 2.55 (ABq, J=14, 2H), 4.20(q, J=7, 1H), 7.7-8.0(m, 4H)
30	$C_{18}H_{22}O_4$	C, 71.50 H, 7.33	71.37 7.54	2990, 1680, 1595 1150	0.88(s, 9H), 1.18(d, J=7, 3H), 1.55(s, 3H), 1.73 and 2.77 (ABq, J=13, 2H), 4.07(q, J=7, 1H), 7.6-8.0(m, 4H)
31	$C_{18}H_{22}O_4$	C, 71.50 H, 7.33	71.58 7.47	2980, 1695, 1600 1155	0.86(s, 9H), 1.32(d, J=7, 3H), 1.47(s, 3H), 1.80 and 2.66 (ABq, J=12, 2H), 4.22(q, J=7, 1H), 7.7-8.1(m, 4H)
32	$C_{17}H_{20}O_4$	C, 70.81 H, 6.99	70.66 7.05	2990, 1685, 1600 1450	0.95(t, J=6, 3H), 1.10(t, J=6, 3H), 1.09(s, 3H), 1.38(s, 3H), 1.6-2.4(m, 4H), 7.6-8.0(m, 4H)
33	$C_{19}H_{24}O_4$	C, 72.12 H, 7.65	71.82 7.76	2980, 1685, 1590 1270, 920, 730	0.89(s, 9H), 1.18(s, 3H), 1.42(s, 3H), 1.75(s, 3H), 1.75 and 2.33(ABq, J=14, 2H), 7.6-7.7(m, 2H), 7.8-7.9(m, 2H)
34	$C_{19}H_{24}O_4$	C, 72.12 H, 7.65	71.22 7.74	2990, 1680, 1590 1270, 1150, 990	0.95(s, 9H), 1.23(s, 3H), 1.39(s, 3H), 1.52(s, 3H),1.73 and 2.75(ABq, J=14, 2H), 7.6-7.8(m, 2H), 7.8-7.9(m, 2H)
35	$C_{24}H_{26}O_4$	C, 76.16 H, 6.93	76.22 7.03	2990, 1700, 1590 1275, 1150, 925	1.13(s, 3H), 1.30(s, 3H), 1.33(s, 3H), 1.40(s, 3H), 1.56 (s, 3H), 2.13 and 2.80(ABq, J=14, 2H), 7.0-7.4(m, 5H), 7.5-7.7(m, 3H), 8.0-8.1(m, 1H)
36	$C_{24}H_{26}O_4$	C, 76.16 H, 6.93	76.02 6.88	2990, 1690, 1600 1150	1.13(s, 3H), 1.20(s, 3H), 1.23(s, 3H), 1.35(s, 3H), 1.36(s, 3H), 2.20 and 3.20(ABq, J=14, 2H), 7.0-7.5(m, 5H), 7.5-8.0(m, 4H)

$$\underset{\underset{\sim}{1}}{} \xrightarrow[\text{acetone}]{h\nu} \underset{\underset{\sim}{2}}{} \qquad (1)$$

$$\underset{\underset{\sim}{3}}{} \xrightarrow{h\nu} \underset{\underset{\sim}{4}}{} \text{ or } \underset{\underset{\sim}{5}}{} \qquad (2)$$

a; $R^1 = R^2 = Me$,

b; $R^1 = R^2 = Et$,

c; $R^1 = Me$, $R^2 = CH_2C(CH_3)$

d; $R^1 = Me$, $R^2 = CH_2C(CH_3)_2Ph$

e; $R^1 = R^2 = Ph$

$$\underset{\underset{\sim}{3a}}{} \xrightarrow[C_6H_6]{h\nu} \underset{\underset{\sim}{6a}}{} + \underset{\underset{\sim}{6b}}{} \qquad (3)$$

$$\underset{\sim}{3a} + \underset{\underset{\sim}{7}}{RCHO} \xrightarrow[C_6H_6]{h\nu} \quad \mathbf{8} \quad + \quad \mathbf{9} \tag{4}$$

$$\underset{\sim}{10} \qquad * = +,- \text{ or } \cdot \qquad \underset{\sim}{11}$$

$$\underset{\sim}{8} + \underset{\sim}{9} \xrightarrow[C_6H_6]{h\nu} \quad \mathbf{12} \quad + \quad \mathbf{13} \tag{5}$$

$$\underset{\sim}{3a} \xrightarrow[RCOR]{h\nu} \quad \mathbf{14} \tag{6}$$
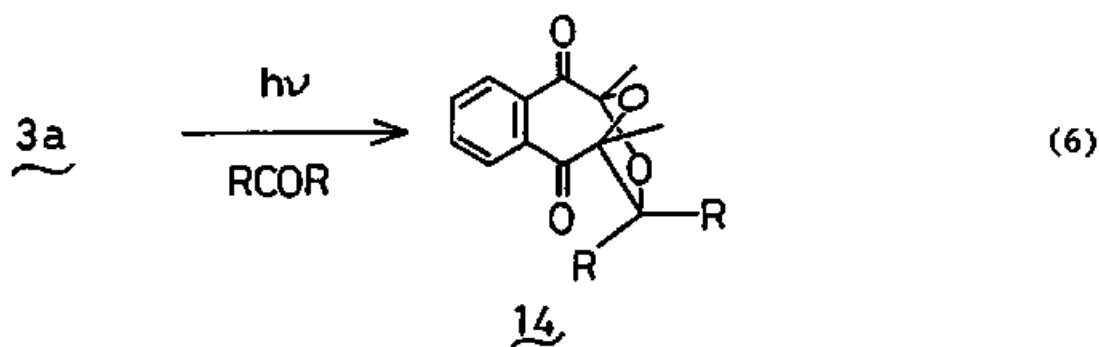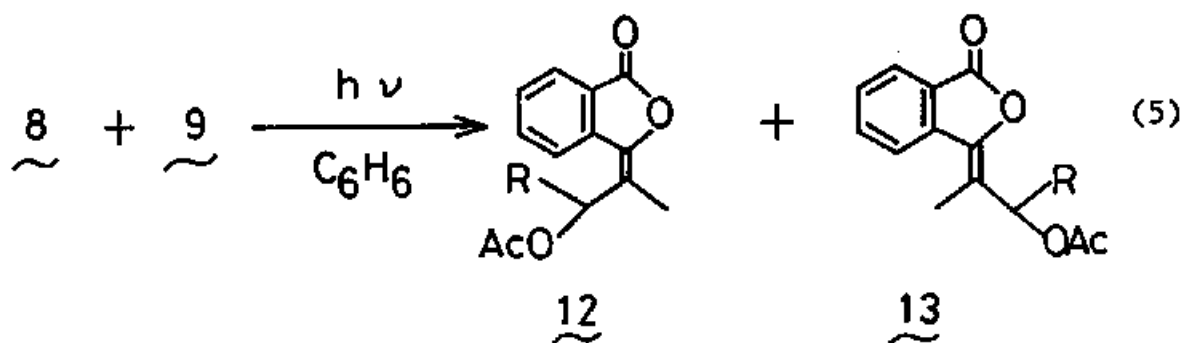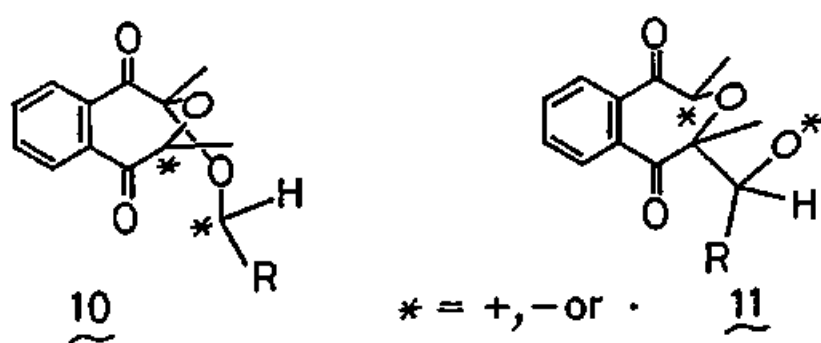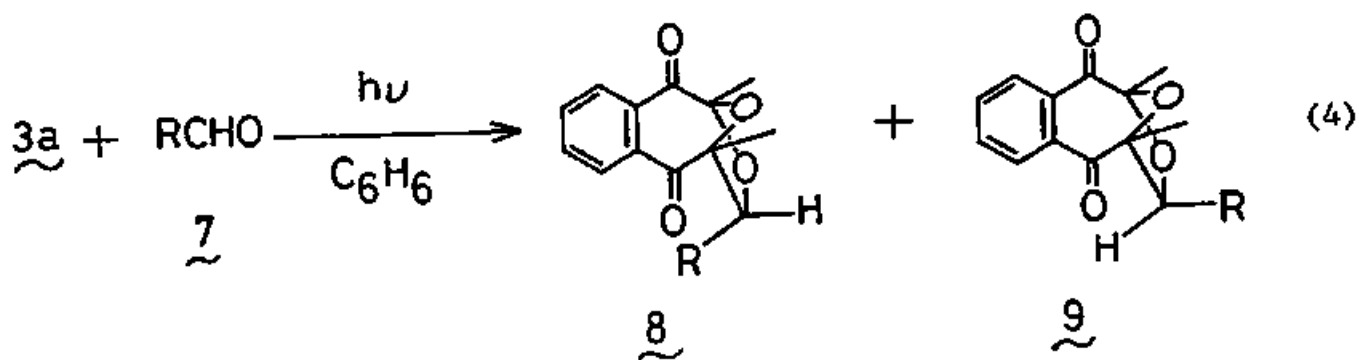
a; $R^1=R^2=Me$, b; $R^1=R^2=Et$, c; $R^1-R^2=(CH_2)_4$,
d; $R^1-R^2=(CH_2)_5$, e; $R^1=Me$, $R^2=Ph$

$$\underset{\underset{\sim}{3a}}{} \quad \xrightarrow[\mathrm{C_6H_6}]{h\nu/O_2} \quad \underset{\underset{\sim}{16}}{} \quad + \quad \underset{\underset{\sim}{17}}{} \qquad (7)$$

Scheme I

$$\underset{\underset{\sim}{3a}}{} \quad \xrightarrow{h\nu} \quad \underset{\underset{\sim}{4a}}{} + \quad \xrightarrow{{}^1O_2} \quad \underset{\underset{\sim}{18}}{}$$

$$\xrightarrow{h\nu \ \text{or} \ \triangle}$$

$$\underset{\underset{\sim}{19}}{} \quad \xrightarrow{\hspace{2cm}} \quad \underset{\underset{\sim}{16}}{} \quad + \quad \underset{\underset{\sim}{17}}{}$$
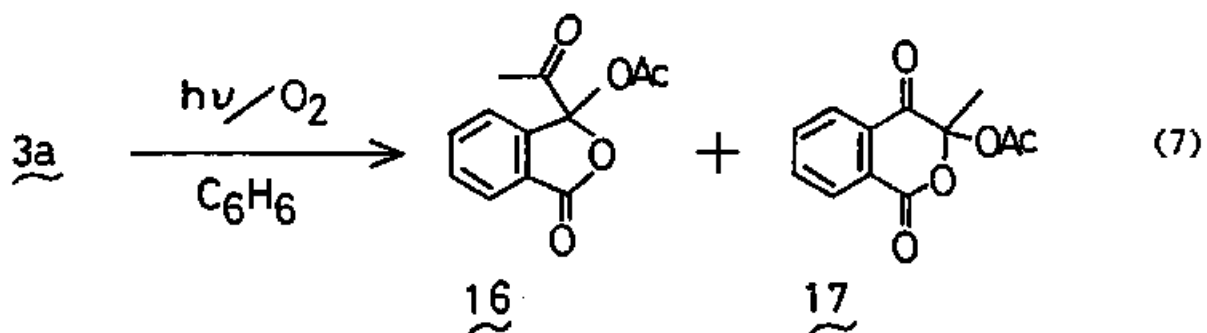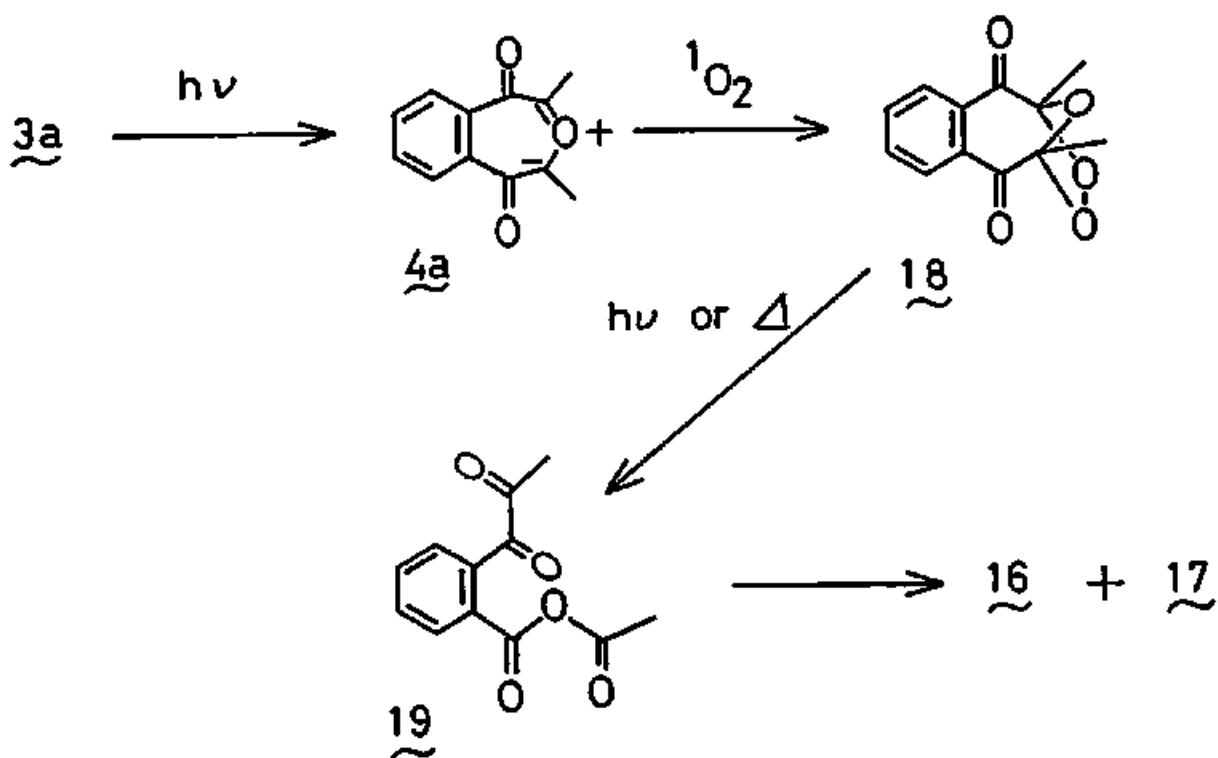
Scheme II
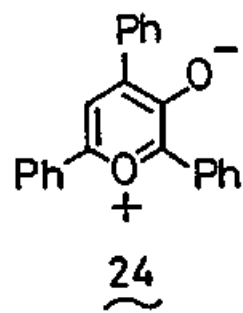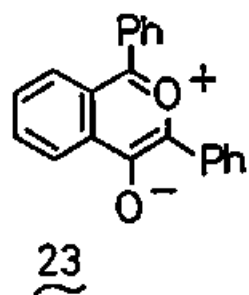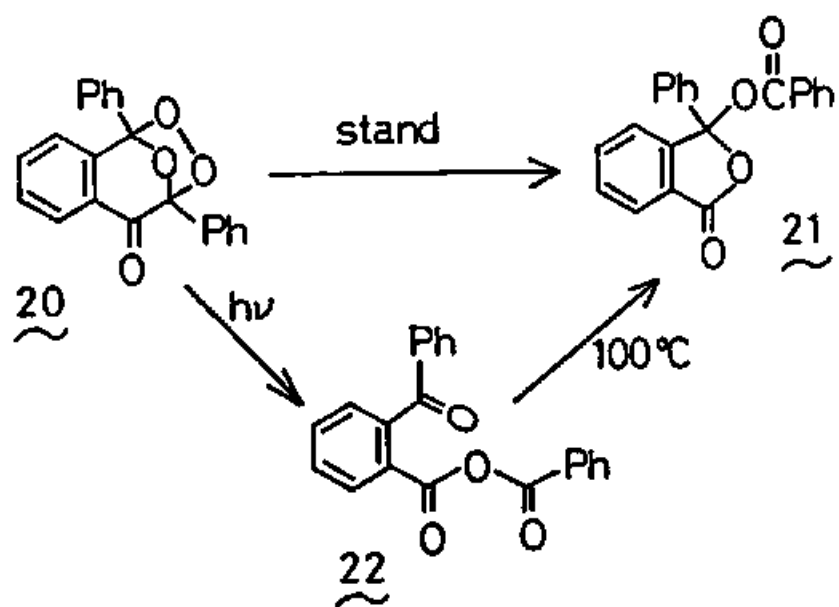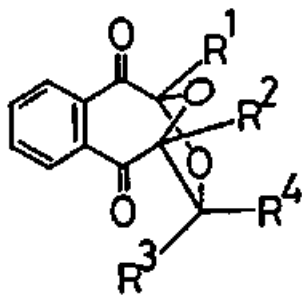
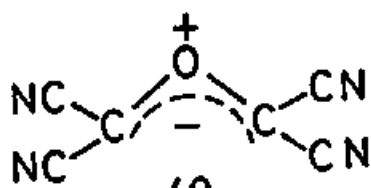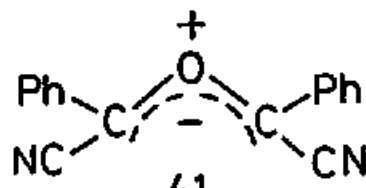|	R^1	R^2	R^3	R^4
25 ;	Et	Et	Me	H
26 ;	Et	Et	H	Me
28 ;	Me	$CH_2C(CH_3)_3$	Me	H
29 ;	Me	$CH_2C(CH_3)_3$	H	Me
30 ;	$CH_2C(CH_3)$	Me	Me	H
31 ;	$CH_2C(CH_3)$	Me	H	Me
32 ;	Et	Et	Me	Me
33 ;	Me	$CH_2C(CH_3)_3$	Me	Me
34 ;	$CH_2C(CH_3)$	Me	Me	Me
35 ;	Me	$CH_2C(CH_3)_2Ph$	Me	Me
36 ;	$CH_2C(CH_3)_2Ph$	Me	Me	Me
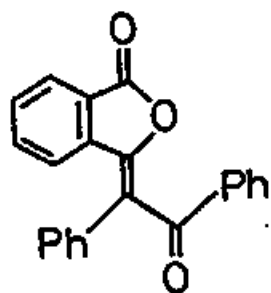
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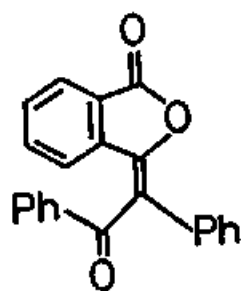
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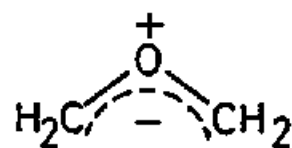
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Photochemistry of Epoxyquinone 6.[1] Norrish Type II Photoreaction of 2,3-Dihydro-2,3-epoxy-1,4-naphthoquinone.

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Photochemical reactions of 2,3-dialkyl substituted or 2-alkyl substituted 2,3-dihydro-2,3-epoxy-1,4-naphthoquinone in which carbonyl group has intramolecularly abstractable γ-hydrogen atoms have been studied. On irradiation, epoxynaphthoquinones 11a-h initially afforded cyclobutanols 12a-h and phthiocol 13a and 13b. The former are Norrish type II cyclization products, while the latter may be formed *via* an allene oxide intermediate which is a direct Norrish type II elimination product. The cyclobutanols 12a-h underwent secondary photo-rearrangement to β-diketones 14a-h and β-alkoxy enones 15a-d,g but 14g and 14h were readily dehydrated on chromatographic separation over silica gel to give indenone derivatives 15g and 15h. Preference for the Norrish type II photoreaction over the generation of the carbonyl ylide or 1,3-diradical was discussed in terms of the rate constants for each process. A tentative mechanism for the novel photochemical reactions of the cyclobuta-nols is proposed.

Considerable attention has been focused in recent years on the photochemistry of small-ring heterocyclic compounds.[2] Among these, investigations of a number of α,β-epoxy ketones 1

have demonstrated that these compounds are photochemically labile and most can be classified into two groups according to their reaction modes; a) C_α-O bond cleavage leading to the formation of a 1,3-diradical $\underline{2}$ which would give a β-diketone $\underline{3}$ by 1,2-alkyl migration of either R^2 or R^3 group, and b) C_α-C_β bond fission leading to the formation of a carbonyl ylide $\underline{4a}$ or 1,3-diradical $\underline{4b}$ which would give a tetrahydrofuran $\underline{5}$ by 1,3-cycloaddition to olefin. Recently, photochemical generation of the carbonyl ylide $\underline{6}$ or 1,3-diradical $\underline{7}$ from several epoxy-naphthoquinones was reported.[3] These reactive intermediates were successfully trapped by olefins,[3a] ketones,[3b] and aldehydes.[3b] However, irradiation of dimethylacrylophenone oxide ($\underline{8a}$) and *trans*-dypnone oxide ($\underline{8b}$) were reported to give the unsaturated keto alcohol $\underline{9a}$ and $\underline{9b}$, respectively, as the major products.[4] The absence of detectable amounts of β-diketo products in those cases is noteworthy. The authors postulated that the reaction proceeds by initial γ-hydrogen abstraction followed by homolytic scission of the oxirane ring. These results suggest the preference of γ-hydrogen abstraction over opening of the oxirane ring [path a) or path b) in Scheme I] in the reaction of triplet aryl ketones. In this paper, the photochemical reaction of 2,3-dialkyl or 2-alkyl substituted 2,3-dihydro-2,3-epoxy-1,4-naphthoquinones in which the carbonyl group has intramolecularly abstractable γ-hydrogen atoms will be described. This paper will reveal that the Norrish type II photoreaction is preferred to the generation of the carbonyl ylide $\underline{6}$ or 1,3-diradical $\underline{7}$.[5]

Results and Discussion

Syntheses of Starting Epoxynaphthoquinones. The syn-
thesis of 2,3-dialkyl-substituted epoxynaphthoquinones 11a-f
was achieved by NaOCl/pyridine epoxidation of 2,3-dialkyl-
substituted 1,4-naphthoquinones 10a-f, which, in turn, were
prepared by the method of Jacobsen.[6] 2-Alkyl-substituted
epoxynaphthoquinones 11g and 11h were prepared by epoxidation
of 2-alkyl-1,4-naphthoquinones 10g and 10h, respectively, with
alkaline hydrogen peroxide.[7]

Photoproducts Analysis. Irradiation of a benzene solu-
tion of 2-methyl-3-(2-methyl)propyl-2,3-dihydro-2,3-epoxy-1,4-
naphthoquinone (11a) (0.02M) with Pyrex-filtered light with up to
65% conversion of reactant followed by separation over silica gel afforded
the cyclobutanol 12a (25%), the phthiocol 13a (17%), the β-
diketone 14a (40%), and the β-alkoxy enone 15a (15%). Structure
assignments for these photoproducts were made on the basis of
characteristic spectral data and elemental analyses. The IR
spectrum of 12a showed characteristic bands at 3400 (hydroxy)
and 1680 (a conjugated ketone) cm^{-1}; the ^{1}H NMR (CDCl$_3$) spectrum
indicated the presence of three methyl groups at δ 0.84, 1.42,
and 1.50 ppm and methylene hydrogens at δ 2.06 and 2.84 (ABq, J=10Hz)
ppm. The ^{13}C NMR (CDCl$_3$) of 12a revealed one ketone carbonyl
at δ 191.9 ppm, four quaternary carbons at δ 78.1, 66.1, 59.4,
and 40.4 ppm, and one methylene carbon at δ 39.0 ppm, besides
three methyl carbons and six aromatic carbons (Figure 1).
2-Hydroxy-3-methyl-1,4-naphthoquinone (13a) was identical with
an authentic sample prepared by the treatment of 2-methyl-2,3-
dihydro-2,3-epoxy-1,4-naphthoquinone (22) with concentrated sul-

furic acid.[8] The IR spectrum of 14a showed characteristic bands at 3450 (hydroxy), 1750 (a five-membered ketone), and 1715 (a conjugated five-membered ketone) cm^{-1}; the ^{1}H NMR (CDCl$_3$) spectrum indicated the presence of three methyl groups at δ 1.06, 1.20, and 1.34 ppm and methylene hydrogens at δ 2.04 and 2.28 (ABq, J=15 Hz) ppm. The ^{13}C NMR (CDCl$_3$) spectrum of 14a revealed the presence of two ketone carbons at δ 208.3 and 198.8 ppm, three quaternary carbons at δ 87.0, 69.7, and 52.4 ppm, one methylene carbon at δ 42.2 ppm, besides three methyl carbons and six aromatic carbons. The stereochemistry of the ring junction of the β-diketone 14a was assigned to be *cis*-fused on the basis of changes in the chemical shifts of its protons on addition of the shift reagent; tris(dipivalomethanato)europium (III) [Eu(DPM)$_3$] (Figure 2).[9] This assignment was confirmed by the fact that 14a did not isomerize at all on treatment with hydrochloric acid in chloroform even at elevated temperature, since the *trans*-isomer would isomerize readily on acid-treatment due to its highly strained structure. The IR spectrum of 15a showed characteristic bands at 3320 (hydroxy) and 1650 and 1635 (a conjugated ketone) cm^{-1}; the ^{1}H NMR (CDCl$_3$) spectrum indicated the presence of three methyl groups at δ 0.82, 1.54, 1.66 ppm and methylene hydrogens adjacent to the oxygen at δ 3.96 and 4.56 (ABq, J=7Hz) ppm. The data of ^{13}C NMR (CDCl$_3$) spectrum of 15a were consistent with the assigned structure; δ 186.4 (s, a conjugated ketone), 176.6 (s, β-carbon of β-alkoxy enone), 109.1 (s, α-carbon of β-alkoxy enone), 83.2(t), 76.4(s), 45.2(s), besides three methyl carbons and six aromatic carbons. The UV (EtOH) spectral properties of 15a also indicated α,β-unsaturated aryl ketone; λ_{max} 315 (ε=

5000) and 292 (ϵ=6150).   Further, reductive acetylation (Zn/ Ac$_2$O) of 15a yielded naphthalene derivative 16a in a yield of 75%.

Controlled experiments revealed that the cyclobutanol 12a and the phthiocol 13a were the primary photoproducts (12a/13a= 10) arising from a type II reaction and upon continued irradiation 12a was transformed into 13a, 14a, and 15a. High-pressure liquid chromatography (HPLC) analysis of the irradiation of 12a (0.015 M) in benzene revealed that the ratio of 13a:14a:15a was constant (1:6.5:2.5) during the irradiation, indicating that no interconversion of either 13a, 14a, or 15a was operative under the reaction conditions (Figure 3). The cyclobutanol 12a was obtained in a higher yield (63%) by irradiating 11a for a suitable time in methanol, where the efficiency of type II reaction was greatly enhanced by biradical solvation but that of the secondary photoreaction of 12a was not so influenced.

Further examples which would support the generality of the preference of the intramolecular γ-hydrogen abstraction over the generation of the carbonyl ylide or 1,3-diradical and succeeding photochemical rearrangement of the cyclobutanol 12 were sought. With this in mind, the photochemical behavior of a number of epoxynaphthoquinones which contain γ-hydrogen atoms was invesigated. In each case, cyclobutanol 12 and phthiocol 13 arising from intramolecular γ-hydrogen atom abstraction and rearranged products arising from cyclobutanol 12 were observed. Irradiation of 2-methyl-3-cyclohexylmethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11b) in benzene gave the cyclobutanol 12b (16%), 13a (12%), the β-diketone 14b (40%), and the β-alkoxy enone 15b (10%). The latter two products were secondary photoproducts

derived from 12b. Similar irradiation of 2-methyl-3-propyl-
2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11c) in benzene gave
the epimeric cyclobutanols 12c-ex (29%) and 12c-en (15%),
13a (10%), the epimeric β-diketones 14c-ex (14%) and 14c-en
(9%), and the epimeric β-alkoxy enones 15c-ex (7%) and 15c-en
(3%). The stereochemistry at C-10 position of 12c was assigned
on the basis of the chemical shifts of methyl protons at C-10.
The methyl protons of 12c-en appeared at higher field (δ 0.80)
due to the shielding effects of benzene ring, compared with
those of 12c-ex appearing at δ 1.42. A separate irradiation of
the cyclobutanol 12c-ex in benzene gave only 14c-ex, 15c-ex,
and 13a and similarly 12c-en gave only 14c-en, 15c-en, and 13a,
indicating that the photorearrangement of 12c to 14c and 15c
proceeds without epimerization of methyl group at C-10.

Irradiation of 2-ethyl-3-methyl-2,3-dihydro-2,3-epoxy-1,4-
naphthoquinone (11d) in benzene led only to poorer yields of type
II photoproducts, accompanied by the formation of many unident-
ified products. On the other hand, the cyclobutanol 12d and
the phthiocol 13a were obtained in 43 and 7% yields, respectively,
by irradiating 11d in benzene-Bu^{t}OH (1:1). Again, the cyclobutanol
12d was found to undergo photochemical rearrangement to the
β-diketone 14d (52%) and the β-alkoxy enone 15d (22%) and the
photoelimination to 13a (9%). In the photochemistry of 11d,
competitive generation of the carbonyl ylide or 1,3-diradical
appeared to be responsible for the lower yields of type II pho-
toproducts. In fact, irradiation of a benzene-Bu^{t}OH (1:1) solu-
tion of 11d (0.05 M) and dimethyl fumarate (0.07 M) resulted in
the formation of a 1:1 mixture of isomeric adducts 17a and 17b

(31%) arising from 1,3-cycloaddition of carbonyl ylide or 1,3-diradical to dimethyl fumarate, along with type II photoproducts, **12d** (24%) and **13a** (4%).

When irradiation of 2-methyl-3-(2,2-diphenyl)ethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (**11e**) was carried out in benzene up to 67% converison, the cyclobutanol **12e** (51%), **13a** (15%), 1,1-diphenylethylene (8%), and the β-diketone **14e** (22%) were obtained. The photochemistry of **12e** stands in contrast to those of **12a-d** in view of the facts that **12e** gave a significant amount of **11e** along with **13a** and **14e** but no sign of the formation of **15e** could be detected (Figure 4). This can be interpreted as a direct evidence for competitive C_1-C_{10} bond rupture leading to the formation of type II biradical, which will produce **11e** by reverse hydrogen tranfer (disproportionation).

Epoxidation of 2-methyl-3-(2-phenyl)propyl-1,4-naphthoquinone (**10f**) gave a 1:1 mixture of diastereoisomeric epoxynaphthoquinones which could be separated by repeated column chromatography over silica gel, giving **11f** (mp 76-78°C) and **11f'** (mp 83.5-84.5°C). Irradiation of either **11f** or **11f'** resulted in the almost same product distribution; **11f** gave the epimeric cyclobutanol **12f-ex** (51%) and **12f-en** (8.5%), **13a** (15%), and the epimeric β-diketones **14f-ex** (16%) and **14f-en** (7%), while **11f'** gave **12f-ex** (61%), **12f-en** (3%), **13a** (14%), **14f-ex** (12%), and **14f-en** (6%). In each case, the corresponding β-alkoxy enone **15f** was not detected in the crude photolysate but 2-phenylpropene was detected by GC analysis in about 10%. The stereochemistry of **12f-ex** and **12f-en** was assigned on the basis of the chemical shifts of methyl protons at C-10. The methyl protons of **12f-ex**

appeared at δ 1.23, while those of <u>12f-en</u> appeared at δ 1.56.
In contrast to the photochemical behaviors of <u>12c-ex</u> and <u>12c-en</u>,
a separate irradiation of <u>12f-ex</u> in benzene gave rise to a 2:1
epimeric mixture of <u>14f-ex</u> and <u>14f-en</u>, along with small amounts
of <u>11f</u> and <u>11f'</u> and <u>13a</u>, suggesting competitive C_1-C_{10} bond
rupture in <u>12f</u>.

The photochemical reactions of 2-alkyl-substituted epoxy-
naphthoquinones <u>11g</u> and <u>11h</u> have also been studied. Irradiation
of 2-(2-methyl)propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone
(<u>11g</u>) in methanol with up to 63% conversion followed by the separation
over silica gel afforded the cyclobutanol <u>12g</u> (52%), 2-hydroxy-
1,4-naphthoquinone <u>13b</u> (2%), the β-alkoxy enone <u>15g</u> (10%), and
the indenone derivative <u>18g</u> (26%). The last product seemed to
arise from the dehydration of the expected β-diketone <u>14g</u>. In
fact, ^{1}H NMR examination of the crude photolysate of <u>12g</u> in
benzene showed no peaks due to <u>18g</u> but instead a set of two methyl
singlets at δ 0.76 and 1.33 and AB quartet at δ 2.15 and 2.68
(J=15Hz) and singlet at δ 3.44, presumably due to <u>14g</u>. On
treatment of this crude photolysate with silica gel in benzene
at room temperature, one observed rapid appearance of ^{1}H NMR
signals due to <u>18g</u> as well as rapid disappearance of the signals
mentioned above. Consequently, the indenone derivative <u>18g</u> is not
a direct photolysis product from <u>12g</u> but is formed from a precursor,
maybe <u>14g</u> , which is readily dehydrated on treatment with silica
gel. Similar irradiation of 2-(2,2-diphenyl)ethyl-2,3-dihydro-
2,3-epoxy-1,4-naphthoquinone (<u>11h</u>) in benzene gave the cyclo-
butanol <u>12h</u> (65%), <u>13b</u> (5%), 1,1-diphenylethylene (4%), and the
β-alkoxy enone <u>14h</u>(30%, determined by ^{1}H NMR). The last product,

which was only detected by ^{1}H NMR spectroscopy [at δ 2.68 and 3.00 (ABq, J=15Hz) and 3.40(s, 1H)], was isolated as the indenone derivative <u>18h</u> (28%) after chromatographic separation over silica gel. No sign of the formation of <u>15h</u> could be detected in this case as well as <u>11e</u>, <u>11f</u>, and <u>11f</u>.

Reaction Mechanism.   The formation of the cyclobutanols <u>12</u> and 2-hydroxy-1,4-naphthoquinones <u>13</u> can be readily accounted for in terms of a type II process. A biradical <u>19</u> is initially formed by γ-hydrogen atom abstraction. Cyclization of the biradical yields the cyclobutanol <u>12</u>, while direct elimination probably results in the formation of the phthiocol <u>13</u>. The preferential cyclization of <u>19</u> is consistent with previous reports for rigid systems, where elimination would produce highly strained bicyclic compounds with bridgehead double bonds, i.g., α-adamantylacetone[10a] and α-adamantylacetophenone.[10b] Mechanistic details of photoelimination to give <u>13</u> have not yet been understood but the formation of <u>13</u> should be correlated with intramolecular γ-hydrogen abstraction because none of <u>13a</u> was detected in the photolysis of 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (<u>11i</u>) or 2-methyl-3-(2,2-dimethyl)propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (<u>11j</u>). Further, it may be said that elimination occurs prior to a possible epoxy-carbinyl rearrangement, judged by the absence of products derived from a radical <u>20</u>. It is proposed that direct elimination of <u>19</u> yields an allene oxide <u>21</u> as a transient intermediate, which undergoes isomerization to <u>13</u>. The absence of <u>22</u> in the reaction mixture appears to imply that the keto-enol tautomerization is

of minor importance in 21. This observation is consistent with the suggestion that allene oxide undergoes facile isomerization to cyclopropanone *via* oxyallyl intermediate.[11] In an expected oxyallyl zwitterion 23 arising from isomerization of 21, intramolecular proton transfer could produce 13. There have been earlier reports in which type II photoelimination results in the formation of highly strained species involving oxygen-containing three-membered ring. Phenyloxirene 29 has been proposed as an intermediate in type II photoelimination of β,γ-epoxy ketone 28,[12] although the intervention of oxirene in this process seems to be rather controversial.[13] Present results imply that type II photoelimination of spiro-α,β-epoxy ketone 30 might provide a transient allene oxide intermediate with hydroxy group. New studies toward such direction are currently in progress.

Quantum yields for disappearance of epoxynaphthoquinones 11a-h in benzene and benzene-Bu^{t}OH (1:1) were determined by using valerophenone as the chemical actinometer.[14] The results are shown in Table 2. The increase in quantum yield with added alcohol can be attributed to biradical solvation, which suppresses reversion of the biradical to ground state epoxynaphthoquinone.[16] Rate constants for γ-hydrogen abstraction were determined by standard Stern-Volmer quenching experiments in degassed benzene solution using naphthalene as the triplet quencher. From the slopes of the linear Stern-Volmer plots ($k_q\tau$) and the assumption that $k_q=5\times10^9$ M^{-1}s^{-1} in benzene solution,[15] values of the triplet lifetime (τ) are obtained. In view of the short triplet lifetime ($\tau < 10^{-8}$s), it is unlikely that radiationless decay competes with γ-hydrogen abstraction. Thus, the triplet lifetime is determined

by the rate of γ-hydrogen abstraction $(1/\tau = k_\delta)$. Lewis' results[10b] for 2-propyl-1-tetralone **33** in benzene and Pr^iOH are included in Table 2 for purposes of comparison. The reactivity of (nπ*) triplet of **11** toward γ-hydrogen abstraction is determined primarily by the γ C-H bond strengh. Inductive effects[16] by electron-withdrawing substituents such as o-acyl group and α-oxyranyl group and less conformational mobility[10b] imposed by the oxirane ring might enhance the triplet reactivity of **11** but the value of k_δ for **11c** was only 37% as much as that of **33**. These results might be simply accounted for in view of lower triplet energy of **11c**, compared with that of **33**. Type II photo-reaction of **11** was quenched by naphthalene $(E_T = 61 \text{ kcal/mol})$ but only inefficiently by biphenyl $(E_T = 66 \text{ kcal/mol})$, indicating the triplet energies of **11** to be significantly lower than those of alkyl phenyl ketones $(E_T = 72-73 \text{ kcal/mol})$.

In contrast to type II photoreaction of **11a-h**, excitation of **11i** or **11j** gives exclusively rise to the generation of the carbonyl ylide or 1,3-diradical, which can be trapped by suitable dipolaro-philes.[3] It is of mechanistic interest to compare the rate of the opening of the oxirane ring (k_o) with that of the γ-hydrogen abstraction (k_δ). In the case of **11d**, the opening of the oxirane ring occurs competitively with type II process. Both processes were quenched by naphthalene with equal efficiency, indicating that they occurred from the same excited state, presumably (nπ*) triplet state. Since both the cyclobutanol **12d** and the 1,3-di-polar cycloadducts **17a** and **17b** are photolabile under the reaction conditions, the chemical yields of **12d** and **17a** and **17b** do not accurately reflect the relative propensities for the type II

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process and the opening of the oxirane ring. However, the
relative product yields suggest the nearly same rate constants
of two processes in triplet 11d. Degassed benzene solutions
0.015 M in 11i or 11j and 0.02 M in cyclohexene containing
various concentrations of naphthalene were irradiated in parallel
with valerophenone actinometer.[17]   Quantum yields for the
formation of the cycloadducts 34i and 34j were 0.35 for 11i
and 0.70 for 11j, respectively. Stern-Volmer plots were linear
to $\phi^0/\phi=6$ for both epoxynaphthoquinones, with slopes ($k_q\tau$) of
99 M^{-1} for 11i and 20 M^{-1} for 11j. With $k_q=5\times10^9$ $M^{-1}s^{-1}$, $1/\tau=$
5.1×10^7 s^{-1} for triplet 11i and 2.5×10^8 s^{-1} for triplet 11j.
If it is assumed that the triplet lifetime of 11i and 11j is
largely determined by the rate of the opening of the oxirane ring
(k_o), the values of $1/\tau$ can be regarded as k_o. The k_o for 11j
is a factor of 5 higher than that for 11i. It thus appears
that there are steric acceleration effects in the opening of
the inner C-C bond of the oxirane ring in epoxynaphthoquinones.
Although how these effects might enhance k_o in 11a-h is not
known, it can be said that values of k_o are much smaller than
those of k_δ on the basis of the amounts of type II photoproducts
which account for nearly all of the products.

The photorearrangement of the cyclobutanol 12 to the β-
diketone 14 and the β-alkoxy enone 15 can be best explained in
terms of a initial C_α-O bond cleavage to give a diradical 24,
followed by migration of benzyl group to the α-carbon (C-migration)
or migration of methylene group to the oxygen (O-migration).
To the best of our knowledge, 1,2-alkyl migration to oxygen atom
is unprecedented in spite of its formal possibility, although

the photochemistry of α,β-epoxy ketones has been studied exten-
sively.[2] A possible explanation for the unprecedented O-migration
may be that the reaction proceeds in such a concerted manner
that the methylene group have to be attached to the back side
lobe of the bond to be cleaved. Thus, C-migration of the
methylene group would be greatly disfavored by reason of
steric factors. If such sort of concerted migration occur,
C-migration of benzyl group would lead to *trans*-isomer of $\underline{14}$.
Unfortunately, because the *cis* stereochemistry of $\underline{14}$ may be
the result of control by thermodynamic factors (the *trans*-isomer
of $\underline{14}$ would be highly strained), no definitive conclusions
relating to the timing of the $\underline{12}$ to $\underline{14}$ and $\underline{15}$ rearrangement
can be drawn at this time.

As for the mechanism of photoelimination to $\underline{13}$ from $\underline{12}$,
one may envion a route involving C_1-C_{10} bond rupture resulting
in the formation of type II biradical $\underline{19}$, which could produce
$\underline{13}$ by elimination. It is the case for the cyclobutanols $\underline{12e}$,
$\underline{12f\text{-}ex}$, and $\underline{12f\text{-}en}$, which, on excitation, give epoxynaphthoqui-
nones by disproportionation of $\underline{19}$ as well as produce $\underline{13a}$.
However, none of the epoxynaphthoquinones $\underline{11a\text{-}d}$ could be
detected in the irradiation of $\underline{12a\text{-}d}$ in benzene even at the early
stage of the reaction. Further, in the case of $\underline{12c\text{-}ex}$ or $\underline{12c\text{-}en}$,
once C_1-C_{10} bond fission occurred, there should be brought
about concomitant epimerization of the methyl group in $\underline{12c}$, $\underline{14c}$,
and $\underline{15c}$. Therefore, there seems to exist, besides C_1-C_{10} bond
fission, an alternative route to $\underline{13a}$ from $\underline{12a\text{-}d}$. Scheme 4
shows a possible route to $\underline{13a}$ from $\underline{12a\text{-}d}$, which begins with
heterolytic C_3-O bond cleavage followed by proton tranfer to

to give an intermediate 36, which finally gives 13a. It is not
unreasonable that the hydroxy group at the C-1 position of 12 will
interact through hydrogen bonding with the oxirane oxygen, which
will become slightly electron-rich on excitation. Thus, the
cyclobutanol 12a was esterified (HClO₄/Ac₂O, at -20°C) and the
photochemistry of the acetate 37a was examined. Irradiation of
37a in benzene afforded only β-diketone acetate 38a in 52% but
neither O-migration product nor elimination product was not
observed. This result seems to suggest an unique role of the
hydroxy group at C-1 in the photochemistry of cyclobutanol.
The strain arising from spiro-fused structure of 12 also appears
to play an important role in its photochemistry; however,
speculation regarding the detailed reaction mechanism is un-
warranted at present.

In summary, type II photoprocess is prefered to generation
of the carbonyl ylide or 1,3-diradical in the photochemistry of
epoxynaphthoquinones which contain γ-hydrogen atoms. Type II
cyclization gives highly strained cyclobutanol in a good yield,
which is transformed into a novel class of polycondensed ring
compounds, while type II elimination presumably gives allene
oxide which undergoes facile isomerization to phthiocol.

Experimental

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi Model 260-10. ^{1}H NMR spectra were recorded on a JEOL PS-100 and chemical shifts are reported in parts per million on the δ scale from internal Me_4Si. ^{13}C NMR spectra were recorded on a JEOL FX-100. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. High pressure liquid chromatography (HPLC) analyses were performed on a JACSO Model FLC A-700, equipped with a UV detector (Model UVIDEC-100). The separations were made on a 500 x 2 mm stainless-steel column packed with JASCO-Pack SS-05 with a water saturated mixture of hexane and ether as the eluent. GC analyses were performed on a Hitachi Model 163, using a 3φ x 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). UV irradiations were carried out in a Pyrex vessel (Eikosha EHB-WF) under an argon atomosphere with an Eikosha 300-W high-pressure Hg lamp.

Preparation of Epoxynaphthoquinones. The epoxynaphthoquinones used were prepared by epoxidation of the corresponding naphthoquinone with NaOCl/pyridine or alkaline H_2O_2.[1,3a] The naphthoquinones were synthesized by the method of Jacobsen.[6] Isolated yields and physical properties are summarized in Table 3 and 4.

Irradiation of 2-methyl-3-(2-methyl)propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11a). A solution of 11a (1.96

g) in 400 mL of benzene was irradiated for 3 h. Separarion of

the products by column chromatography gave 11a(686 mg), 3,10,

10-trimethyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-

1-ol-4-one (cyclobutanol) (12a) (319 mg, 25%), 2-hydroxy-3-

methyl-1,4-naphthoquinone (phthiocol) (13a) (167 mg, 8%),

2,10,10-trimethyl-1,2-propanoindan-1-ol-3,8-dione (β-diketone)

(14a) (510 mg, 40%), and 3,3,9-trimethyl-2,3,3a, 8-tetrahydro-

naphtho[1,2-b]furan-3a-ol-8-one . (β-alkoxy enone) (15a)

(191 mg, 15%).

Reductive Acetylation of the β-alkoyx enone 15a. A solution

of 15a (70 mg) and anhydrous NaOAc (130 mg) and Zn dust(700 mg)

in 5mL of acetic anhydride was refluxed for 30 min. The react-

ion mixture was poured into 50 mL of saturated $NaHCO_3$ solution

and extracted with two portions of CH_2Cl_2 (50 mL), and the

organic extracts were washed with water before being dried

over Na_2SO_4. Removal of the solvent afforded crude product,

which was purified by short column , giving 16a (58 mg, 75%).

8-Acetoxy-3,3,9-trimethyl-2,3-dihydro-naphthaleno[1,2-b]-

furan (16a); mp 96-98°C; IR(KBr) 2940, 1750(ester C=O), 1360,

1200, 1190, 1075, and 760 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 1,58(s, 6H), 2.18(s,3H),

2.44(s, 3H), 4.34(s, 2H), and 7.2-8.0(m, 4H); ^{13}C NMR(CDCl$_3$) δ

10.0(q), 20.5(q), 27.2(q), 43.8(s), 85.5(t), 114.8(s), 121.9(d),

122.2(d), 122.9(d), 123.2(s), 125.3(s), 125.9(d), 128.7(s),

144.8(s), 156.2(s), and 168.4(ester C=O).

Irradiation of 2-methyl-3-(2-cyclohexyl)ethyl-2,3-dihydro-

2,3-epoxy-1,4-naphthoquinone (11b).   A solution of 11b (2.28

g) in 400 mL of benzene was irradiated for 3 h. Separation of

the products by column chromatography gave 11b(1.32 g), 3-methyl

1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-1-ol-4-one-10-spirocyclohexane (cyclobutanol) (12b) (153 mg, 16%), 13a (108 mg, 17%), 2-methyl-1,2-propanoindan-1-ol-3,8-dione-10-spirocyclohexane (β-diketone) (14b) (383 mg, 40%), and 9-methyl-2,3,3a,8-tetrahydro-naphtho[1,2-b]furan-3a-ol-8-one-spiro-cyclohexane (β-alkoxy enone) (15b) (96 mg, 10%).

Irradiation of 2-methyl-3-propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11c). A solution of 11c (1.85 g) in 400 mL of benzene was irradiated for 3 h. Separation of the products by column chromatography gave 11c (684 mg), 10β-dimethyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-1-ol-4-one (cyclobutanol) (12c-ex) (338 mg, 29%), 3,10α-dimethyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-1-ol-4-one (cyclobutanol) (12c-en), (175 mg, 15%), 13a(96 mg, 10%), 2,10β-dimethyl-1,2-propanoindan-1-ol- 3,8-dione (β-diketone) (14c-ex) (164 mg, 14%), 2,10α-dimethyl-1,2-propanoindan-1-ol-3,8-dione (β-diketone) (14c-en) (105 mg, 9%), 3β,9-dimethyl-2,3,3a,8-tetrahydro-naphtho[1,2-b]furan-3a-ol-8-one (β-alkoxy enone) (15c-ex) (82 mg, 7%), and 3α,9-dimethyl-2,3,3a,8-tetrahydro-naphtho-[1,2-b]furan-3a-ol-8-one(β-alkoxy enone) (15c-en) (35 mg, 3%).

Irradiation of a solution of 12c-ex (100 mg) in 25 mL of benzene gave 13a (8 mg, 10%), 14c-ex (35 mg, 35%), and 15c-ex (17 mg, 17%). On the other hand, irradiation of a solution of 12c-en (100 mg) in 25 mL of benzene afforded 13a (8 mg, 10%), 14c-en (45 mg, 45%), and 15c-en (12 mg, 12%).

Irradiation of 2-ethyl-3- methyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11d). A solution of 11d (1.735 g) in 200 mL of benzene and 200 mL of Bu^{t}OH was irradiated for 1 h.

Separation of the products by column chromatography gave 11d (226 mg), 3-methyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-1-ol-4-one (cyclobutanol) (12d) (649 mg, 43%), and 13a (92 mg, 7%).

Irradiation of the cyclobutanol 12d (300 mg) in 25 mL of benzene for 2 h followed by separation over silica gel gave 2-methyl-1,2-propanoindan-1-ol-3,8-dione (β-diketone) (14d) (156 mg, 52%), 9-methyl-2,3,3a,8-tetrahydro-naphtho[1,2-b]-furan-3a-ol-8-one (β-alkoxy enone) (15d) (66 mg, 22%), and 13a (34 mg, 13%).

Irradiation of 11d in the Presence of Dimethyl Fumarate. A solution containing 11d (270 mg) and dimethyl fumarate (250 mg) in benzene-Bu^{t}OH (1:1, 25 mL) was irradiated for 3 h. After removal of the solvent, resulting residue was chromatographed over silica gel. Products were 12d (65 mg, 24%), 13a (11 mg, 4%), 6-ethyl-9-methyl-7α,8β-dimethoxycarbonyl-6,7,8,9-tetrahydro-6α,9α-epoxy-benzocycloocten-5,10-dione 17a (68 mg, 15%), and 6-ethyl-9-methyl-7β,8α-dimethoxycarbonyl-6,7,8,9-tetrahydro-6α,9α-epoxy-benzocycloocten-5,10-dione 17b (72 mg, 16%). 17a; mp 98-99°C; IR(KBr) 1735, 1695, 1685, 1590, 1440, cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 1.12(t, J=6Hz, 3H), 1.72(s, 3H), 2.44(m, 2H), 3.54 and 3.77(ABq, J=7Hz, 2H), 3.65(s, 3H), 3.77(s, 3H), 7.5-8.0(m, 4H). Anal. Calcd for C$_{19}$H$_{20}$O$_7$: C, 66.27; H, 5.85%. Found: C, 66.43; H, 5.99%. 17b; mp 76-78°C; IR(KBr) 1740, 1735, 1690, 1680, 1440 cm^{-1}; ^{1}H NMR(CDCl$_3$)δ 1.22(t, J=6Hz, 3H), 1.44(s, 3H), 2.55(m, 2H), 3.45 and 3.65 (ABq,J=7Hz, 2H), 3.65 (s, 3H), 3.88(s, 3H), and 7.5-8.0(m, 4H). Anal. Calcd. for C$_{19}$H$_{20}$O$_7$: C, 66.27; H, 5.85%. Found: C, 66.09; H, 5.77%.

Irradiation of 2-methyl-3-(2,2-diphenyl)ethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11e). A solution of 11e (2.96 g) in 400 mL of benzene was irradiated for 3 h. Separation of the products by column chromatography gave 11e (681 mg), 3-methyl-10,10-diphenyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethano-naphthalen-1-ol-4-one (cyclobutanol) (12e) (1.011 g, 51%), 13a (152 mg, 15%), 2-methyl-10,10-diphenyl-1,2-propanoindan-1-ol-3,8-dione (β-diketone) (14e) (436 mg, 22%).

Irradiation of 2-methyl-3-(2-phenyl)propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11f; mp 76-78°C). A solution of 11f (2.46 g) in 400 mL of benzene-Bu^{t}OH (1:1) was irradiated for 1 h. Separation of the products by column chromatography gave 11f(867 mg),11f'(133 mg), 3,10α-dimethyl-10β-phenyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-1-ol-4-one(cyclobutanol) (12f-ex) (740 mg, 51%), 3, 10α-dimethyl-10β-phenyl-1,2,3,4-tetrahydro-naphthalen-1-ol-4-one (cyclobutanol)(12f-en)(123 mg, 8.5%), 13a(134mg, 15%), 2,10β-dimethyl-10α-phenyl-1,2-propano-indan-1-ol-3,8-dione (β-diketone) (14f-ex) (232 mg, 16%), and 2,10α-dimethyl-10β-phenyl-1,2-propanoindan-1-ol-3,8-dione (β-diketone) (14f-en)(102 mg, 7%).

Irradiation of 2-methyl-3-(2-phenyl)propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11f'; mp 83.5-84.5°C). A solution of 11f' (2.42 g) in 400 mL of benzene-Bu^{t}OH (1:1) was irradiated for 1 h. Separation of the products by column chromatography gave 11f (143 mg), 11f'(801 mg), 12f-ex(900 mg, 61%), 12f-en (118 mg, 8%), 13a(127 mg, 14%), 14f-ex (177 mg, 12%) and 14f-en(89 mg, 6%).

Irradiation of a solution of 100 mg of 12f-ex in 25 mL of

benzene for 1 h gave <u>11f</u> (4 mg, 4%), <u>11f</u>'(3 mg, 3%), <u>13a</u> (3 mg, 5%), <u>14f-ex</u>(22 mg, 22%), and <u>14f-en</u>(43 mg, 43%).

Irradiation of 2-(2-methyl)propyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (<u>11g</u>). A solution of <u>11g</u> (1.85 g) in 400 mL of benzene was irradiated for 3 h. Separation of the products by column chromatography gave <u>11g</u> (961 mg), 10,10-dimethyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-1-ol-4-one (cyclobutanol) (<u>12g</u>) (107 mg, 12%), 2-hydroxy-1,4-naphthoquinone (<u>13b</u>) (87 mg, 12%), 3,3-dimethyl-2,3,3a,8-tetra-hydro-naphtho[1,2-b]furan-3a-ol-8-one (β-diketone) (<u>15g</u>) (124 mg, 14%), 8,8-dimethyl-2,3-propanoinden-1,10-dione (<u>18g</u>) (196 mg, 24%). On the other hand, irradiation of <u>11g</u> in methanol gave <u>12g</u> (606 mg, 52%), <u>13b</u>(19 mg, 2%), <u>15g</u>(117 mg, 10%), and <u>18g</u> (279 mg, 26%).

Reductive acetylation of the β-alkoxy enone <u>15g</u>.
A solution of <u>15g</u> (70 mg) and anhydrous NaOAc (130 mg) and Zn dust (700 mg) in 5mL of acetic anhydride was refluxed for 30 min. The reaction mixture was poured into 50 mL of saturated NaHCO$_3$ solution and extracted with two portions of CH$_2$Cl$_2$ (50 mL), and the organic extracts were washed with water before being dried over Na$_2$SO$_4$. Removal of the solvent afforded crude product, which was purified by short column, giving <u>16g</u> (50 mg, 68%).

8-Acetoxy-3,3-dimethyl-2,3-dihydro-naphtho[1,2-b]furan (<u>16g</u>); colorless oil; IR(CCl$_4$) 2940, 1760,1620, 1360, 1190, 1135, and 755 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.60(s, 6H), 2.42(s, 3H), 4.37 (s, 2H), 6.91(s, 1H), 7.2-8.1(m, 4H). Anal. Calcd. for C$_{16}$H$_{16}$O$_3$: C, 74.98; H, 6.29%. Found: C, 74.68; H, 6.18%.

Irradiation of 2-(2,2-diphenyl)ethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (11h).   A solution of 11h (2.85 g) in 400 mL of benzene was irradiated for 3 h. Separation of the products by column chromatography gave 11h (712 mg), 13b (57 mg, 5%), 10,10-diphenyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethano-naphthalen-1-ol-4-one (cyclobutanol) (12h) (1.39 g, 65%), 8,8-diphenyl-2,3-propanoinden-1,10-dione (18h) (568 mg, 28%).

Quantum Yield Determination.   γ-Valerophenone actinometry was used for quantum yield determination. The 313 nm line was isolated with a filter solution containing 0.002 M

K_2CrO_4 in a 1% aquous soltion of K_2CO_3. The degree of the reaction was determined by GC analysis relative to known concentration of alkane internal standard.

General Procedure for Acetylation of the β-Diketones 14.

A solution of 14 (100 mg) in 20 mL of acetic anhydride was cooled to -20°C, added three drops of $HClO_4$ cautiously, and then immediately poured into 100 mL of ice-water. The reaction mixture was extracted with two portions of CH_2Cl_2 and the organic extract was washed with water. Removal of the solvent afforded a yellow oil, which was separated by column chromatography over silica gel. Yields and physical properties are summarized in Table 8.

Acetylation of the Cyclobutanol 12a.   A solution of 12a (480 mg) in 30 mL of acetic anhydride was cooled to -20°C, added three drops of $HClO_4$ cautiously, and then immediately poured into 200 mL of ice-water. The reaction mixture was extracted with two portions of CH_2Cl_2 and the organic extracts was washed with water. After removal of the solvent, the resulting oil

was chromatographed over silica gel giving colorless crystals of 1-acetoxy-3,10,10-trimethyl-1,2,3,4-tetrahydro-2,3-epoxy-1,2-ethanonaphthalen-4-one (37a) (167 mg, 30%). 37a; mp 114-115°C; IR(KBr) 2960, 1760(ester C=O), 1700(ketone C=O), 1380, 1220, and 1035 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.85(s, 3H), 1.48(s, 3H), 1.52(s, 3H), 2.05(s, 3H), 2.10 and 2.86 (ABq, J=12Hz, 2H), 7.0-7.6(m, 3H), and 8.0-8.2(m, 1H).

Irradiation of 37a in Benzene Solution.   A benzene solution of 37a (100 mg) was irradiated for 3h. After removal of the solvent, the resulting residue was separated over silica gel. Major product was the β-diketone-acetate 38a (52 mg, 52%) and small amount (13 mg) of unidentied product was also obtained.

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9, Although in the preliminary paper, ref. 5a), we erroneously assigned a *trans*-fused structure for β-diketone, it should be corrected to the *cis*-fused. In ref. 5a), the assignment was only based on the comparison of the chemical shift of methyl protons of <u>14e</u> (at δ 1.36) with that of its acetate (at δ 1.36).

However, acetylation of <u>14e</u> was carried out under acidic conditions ($HClO_4/Ac_2O$), where *trans*-<u>14e</u> should isomerize to thermodynamically stable *cis*-<u>14e</u>. Further, the comparison of the chemical shifts of methyl protons of <u>14</u> with those of their acetates in the series appeared to provide support for the *cis*-fused structure (Figure 5).

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17. The total amounts of 1,3-dipolar cycloadducts <u>34i</u> and <u>34j</u> and their secondary photoproducts accounted for neary all of the products produced in the reaction of <u>11i</u> and <u>11j</u> with cyclohexene. Triplet states of <u>11i</u> and <u>11j</u> were slightly quenched by electron-rich olefins but 0.02M of cyclohexene affected the triplet lifetimes of <u>11i</u> and <u>11j</u> at most less than 2%. Osuka, A.; Suzuki, H.; Maruyama, K. Unpublished results.

Table 1.　　　Type II Photoreaction of Epoxynaphthoquinones

Run	Reactant	Solvent	Conv. (%)	Product Distribution (%)[a]			
				12	13	14	15
1	11a	C_6H_6	20	73	8[b]	12	5
2	11a	C_6H_6	65	25	17[b]	40	15
3	11a	MeOH	78	63	6[b]	15	7
4	11b	C_6H_6	42	16	12[b]	40	10
5	11c	C_6H_6	63	44[c]	10[b]	25[d]	10[e]
6	11d	C_6H_6-Bu^tOH[f]	87	43	7[b]	g)	g)
7	11e	C_6H_6	67	51	15[b]	22	h)
8	11f	C_6H_6-Bu^tOH	59	59.5[i]	15[b]	23[j]	h)
9	11f'	C_6H_6-Bu^tOH	61	69[k]	14[b]	18[l]	h)
10	11g	C_6H_6	48	12	12[m]	24[n]	14
11	11g	MeOH	63	52	2[m]	26[n]	10
12	11h	C_6H_6	75	65	5[m]	28[n]	h)

a), Isolated yields based on the amounts of consumed 11. b), 13a. c), 12c-ex/12c-en=1.93. d) 14c-ex/14c-en=1.56. e), 15c-ex/15c-en=2.33. f), C_6H_6/Bu^tOH=1. g), Not determined. h), Not detected.

i), 12f-ex/12f-en=0.17. j), 14f-ex/14f-en=0.44. k), 12f-ex/12f-en=0.13. l), 14f-ex/14f-en=0.5.

m), 13b. n), Isolated yields as the indenone derivatives 18.

Table 2.　　Quantum Yields and Kinetic Data for
the Type II Photoreaction of Epoxynaphthoquinones.

Epoxynaphtho-quinones[a]	ϕ [b]		$k_q\tau (M^{-1})$ [c]	$10^{-8} 1/\tau (s^{-1})$
	C_6H_6	C_6H_6-Bu^{t}OH		
__11a__	0.082	0.49	13	3.7
__11b__	0.085		5.4	9.1
__11c__	0.11		23	2.2
__11d__	0.27		58	0.86
__11e__	0.18	0.32	3.8	13
__11f__	0.23	0.60	7.5	6.7
__11f'__	0.25		7.2	7.1
__11g__	0.067		10	5.0
__11h__	0.36	0.54	2.8	18
__33__[d]	0.12	0.39[e]	8.5 [f]	5.9

a) Concentration of epoxynaphthoquinone, *ca.* 0.015M. b) Quantum
yields for the disappearance of epoxynaphthoquinones, ± 10%.
c) Least-squares slope of linear Stern-Volmer plots in benzene
 solution using naphthalene quencher, ± 10%. d) From ref. 10b.
e) Quantum yield in Pr^{i}OH.　f) Using *trans*-1,3-pentadiene as
 triplet quencher.

Table 3 Physical Properties of 1,4-Naphthoquinones 10

Compound	Yield(%)[a]	mp(°C)	Elemental Analysis Calcd.(%)	Found(%)	IR(KBr)	^{1}H NMR(CDCl$_3$)
10a	66	oil	C, 78.92	78.99	2940, 1660, 1600,	0.96(d, J=6Hz, 6H), 1.90(m, 1H), 2.06(s, 3H),
			H, 7.06	9.98	1290, 710	2.54(d, J=6Hz, 2H), 7.5-7.6(m, 2H),
						7.9-8.0(m, 2H)
10b	41	68-69.5	C, 80.56	80.72	2910, 1660, 1650,	0.9-1.9(m, 11H), 2.2(s, 3H), 2.58(d, J=6Hz,
			H, 7.51	7.77	1600, 1300, 710	2H), 7.6-7.8(m, 2H), 8.0-8.2(m, 2H)
10c	62	60-61	C, 78.48	78.63	2960, 1670, 1630,	1.02(t, J=6Hz, 3H), 1.54(m, 2H), 2.08
			H, 6.59	6.72	1600, 1300, 730,	(s, 3H), 2.60(t, J=6Hz, 2H), 7.6-7.7
						(m, 2H), 7.9-8.1(m, 2H)
10d	43	67-68	C, 77.98	78.04	2960, 1660, 1620,	1.10(t, J=6Hz, 3H), 2.15(s, 3H), 2.63
			H, 6.04	6.11	1600, 1300, 710	(q, J=6Hz, 2H), 7.6-7.7(m, 2H),
						7.9-8.1(m, 2H)
10e	62	114-115	C, 85.20	85.35	1660, 1600, 1300,	1.74(s, 3H), 3.38(d, J=7Hz, 2H), 4.27
			H, 5.72	5.98	700,	(t, J=7Hz, 1H), 7.2-7.3(m, 10H), 7.6-7.7
						(m, 2H), 8.0-8.1(m, 2H)
10f	52	72-74	C, 82.73	92.99	2960, 1660, 1600,	1.35(d, J=6Hz, 3H), 1.90(s, 3H), 2.7-3.1(m,
			H, 6.25	6.33	1310, 710	3H), 7.1-7.2(m, 5H), 7.6-8.1(m, 4H)
10g	61	oil	C, 78.48	78.33	2960, 1670, 1600	0.98(d, J=6Hz, 6H), 1.95(m, 1H), 2.50(d, J=
			6.59	6.41	1300, 1270, 780,	6Hz, 2H), 6.75(s, 1H), 7.6-8.2(m, 4H)
10h	53	97.5-98	C, 85.18	85.03	1660, 1600, 1300,	3.22(d, J=8Hz, 2H), 4.30(t, J=8Hz, 1H),
			H, 5.36	5.25	720	6.35(s, 1H), 7.0-7.2(m, 10H), 7.4-8.0(m, 4H)

Compound	Yield(%)	mp(°C)	Elemental Analysis Calcd.(%)	Found(%)	IR(KBr)	^{1}H NMR(CDCl$_3$)
11a	87	56-57	C, 73.75	73.74	2960, 1695, 1600	0.98(d, J=4Hz, 3H), 1.01(d, J=4Hz, 3H), 1.72(s, 3H),
			H, 6.60	6.71	1310, 710	1.9-2.2(m, 3H), 7.6-7.8(m, 2H), 7.9-8.0(m, 2H).
11b	92	78-79	C, 76.03	76.12	2940, 1700, 1600,	0.9-2.2(m, 13H), 1.7(s, 3H), 7.6-8.1(m, 4H)
			H, 7.09	7.02	1330, 1310, 710	
11c	84	oil	C, 73.02	73.11	2950, 1700, 1590,	0.98(t, J=6Hz, 3H), 1.63(s, 3H), 1.3-1.9(m, 2H),
			H, 6.13	6.20	1310, 710	2.0-2.3(m, 2H), 7.6-7.8(m, 2H), 7.9-8.0(m, 2H)
11d	.87	37-37.5	C, 72.21	72.24	3020, 2960, 1700,	1.10(t, J=7Hz, 3H), 1.7(s, 3H), 1.6-2.5(m, 2H),
			H, 5.59	5.62	1600, 1300, 710	7.6-7.8(m, 2H), 7.9-8.0(m, 2H)
11e	92	128-128.5	C, 81.50	81.08	1695, 1600, 1310	1.18(s, 3H), 2.62(dd, J=10, 14Hz, 1H), 3.05(dd, J=5,
			H, 5.47	5.63	710	14Hz, 1H), 4.50(dd, J=5, 10Hz, 1H), 7.0-7.3(m, 10H),
						7.6-7.8(m, 2H), 7.8-8.0(m, 2H)
11f	41	76-78	C, 78.41	78.44	2950, 1700, 1600,	1.08(s, 3H), 1.40(d, J=7Hz, 3H), 1.98(dd, J=10, 14Hz,
			H, 5.92	5.99	1300, 720	1H), 2.66(dd, J=6, 14Hz, 1H), 3.32(dd, J=6, 10Hz, 1H),
						7.1-7.3(m, 5H), 7.6-7.8(m, 2H), 7.9-8.0(m, 2H)
11f'	39	83.5-84.5	C, 78.41	78.44	2950, 1695, 1600,	1.31(d, J=7Hz, 3H), 1.74(s, 3H), 2.4-2.5(m, 2H),
			H, 5.92	5.88	1300, 710	3.16(m, 1H), 7.1-7.3(m, 5H), 7.6-7.8(m, 2H), 7.9-8.0
						(m, 2H)
11g	62	oil	C, 73.02	73.15	2950, 1700, 1590,	0.94(d, J=6Hz, 3H), 0.98(d, J=6Hz, 3H), 1.53(dd, J=
			H, 6.13	6.21	1300, 720	6, 15Hz, 1H), 1.95(m, 1H), 2.33(dd, J=5, 15Hz, 1H),
						3.81(s, 1H), 7.5-8.0(m, 4H)
11h	73	116-117	C, 81.34	81.58	1700, 1600, 1500,	2.12(dd, J=10,12Hz, 1H), 3.14(s, 1H), 3.37(dd, J=
			H, 5.12	5.08	1300, 710	6, 12Hz, 1H), 4.35(dd, J=6, 10Hz, 1H), 7.0-7.3(m, 10H),
						7.6-8.0(m, 4H)

Table 4　　　　Physical Properties of Epoxynaphthoquinones 11

Table 5.   Physical properties of Cyclobutanols 12

Compound	mp(°C)	Elemental Analysis Calcd.(%)	Found(%)	IR(KBr)	^{1}H NMR(CDCl$_3$)
12a	143-144	C, 73.75 H, 6.60	73.57 6.64	3480, 2980, 1680, 1600, 1305, 770	0.84(s, 3H), 1.42(s, 3H), 1.50(s, 3H), 2.06 and 2.84(ABq, J=10Hz, 2H), 7.1-7.5(m, 3H), 7.9(m, 1H)
12b	159-161	C, 76.03 H, 7.09	76.22 7.21	3500, 2940, 1675, 1600, 750	1.49(s, 3H), 0.9-2.0(m, 10H), 2.21 and 2.62(ABq, J=11Hz, 2H), 7.3-7.7(m, 3H), 8.0(m, 1H)
12c-ex	62-65	C, 73.02 H, 6.13	73.23 6.07	3500, 2950, 1680, 1600, 760	1.39(d, J=7Hz, 3H), 1.53(s, 3H), 2.3-2.5(m, 3H), 7.2-7.6(m, 3H), 8.0(m, 1H)
12c-en	98-101	C, 73.02 H, 6.13	73.18 6.08	3480, 2970, 1685, 1595, 750,	0.81(d, J=7Hz, 3H), 1.66(s, 3H), 1.90(m, 1H), 2.66(m, 1H), 3.23(m, 1H), 7.2-7.6(m, 3H), 8.1(m, 1H)
12d	107-108.5	C, 72.21 H, 5.59	72.26 5.65	3480, 3000, 2950, 1675, 1600, 1200	1.51(s, 3H), 2.0-3.3(m, 4H), 7.3-7.6(m, 3H), 8.1(m, 1H)
12e	198	C, 81.50 H, 5.47	81.06 5.82	3460, 2950, 1670, 1595, 740, 690	1.53(s, 3H), 3.42 and 3.88(ABq, J=10Hz, 2H), 6.9(m, 10H), 7.2-7.8 (m, 3H), 7.9(m, 1H)
12f-ex	185-187	C, 78.41 H, 5.92	78.36 5.96	3460, 2950, 1680, 1600, 1450, 740	1.23(s, 3H), 1.60(s, 3H), 2.33 and 3.66(ABq, J=13Hz, 2H), 7.2-7.6(m, 8H), 8.0-8.2(m, 1H)
12f-en	142-143	C, 78.41 H, 5.92	78.44 5.87	3460, 2940, 1695, 1600, 740	1.56(s, 3H), 1.83(s, 3H), 3.00and 3.20(ABq, J=12Hz, 2H), 6.8-7.1(m, 5H), 7.2-7.8(m, 4H)
12g	111-111.5	C, 73.02 H, 6.13	72.88 6.03	3450, 1670, 1600, 1295, 760	0.92(s, 3H), 1.43(s, 3H), 2.16 and 3.00(ABq, J=12Hz, 2H), 7.2-7.8(m, 3H), 8.0(m, 1H)
12h	155-157	C, 81.34 H, 5.12	81.58 5.08	3450, 1680, 1605, 1295, 750, 700	3.64(s, 1H), 3.52 and 3.95(ABq, J=10Hz, 2H), 6.9-8.0(m, 14H)

Table 6   Physical Properties of β-Diketones 14 and Indenones 18

Compound	mp(°C)	Elemental Analysis Calcd.(%) Found(%)		IR(KBr)	^{1}H NMR(CDCl$_3$)
14a	196	C, 73.75	73.49	3450, 1750, 1715,	1.06(s, 3H), 1.20(s, 3H), 1.34(s, 3H), 1.40(broad, 1H),
		H, 6.60	6.82	1200, 1070	2.04 and 2.28(ABq, J=15Hz, 2H), 7.3-7.8(m,4H)
14b	147-149	C, 76.03	76.22	3420, 2910, 1740,	1.36(s, 3H), 2.08 and 2.63(ABq, J=16Hz, 2H), 2.55(broad,1H),
		H, 7.07	7.01	1685, 1600, 1250	1.0-2.0(m, 10H), 7.5-7.9(m, 4H)
14c-ex	138-139.5	C, 73.02	73.14	3340, 2960, 1755,	1.26(s, 3H), 1.30(d, J=7Hz, 3H), 1.70(dd, J=4, 17Hz, 1H),
		H, 6.13	6.16	1710, 1055, 780	2.30(m, 1H), 2.32(dd, J=8, 17Hz, 1H), 7.5-7.9(m, 4H)
14c-en	122-125	C, 73.02	73.31	3500, 2960, 1760,	1.20(d, J=7Hz, 3H), 1.33(s, 3H), 2.21(d, J=6Hz, 2H),
		H, 6.13	6.00	1695, 1080, 770	2.65(m, 1H), 7.6-7.9(m, 4H)
14d	133-134	C, 72.21	72.16	3450, 1750, 1700,	1.27(s, 3H), 1.9-2.8(m, 4H), 7.4-7.9(m, 4H)
		H, 5.59	5.57	1050, 760	
14e	220-222	C, 81.50	81.46	3400, 1745, 1705,	1.36(s, 3H), 3.08(s, 2H), 6.75(m, 1H), 7.1-7.9(m, 13H)
		H, 5.47	5.52	1100	
14f-ex	177-178	C, 78.41	78.47	3450, 1750, 1690,	1.13(s, 3H), 1.30(s, 3H), 2.41 and 3.43(ABq, J=16Hz, 2H)
		H, 5.92	5.96	1285, 755	7.4-7.9(m, 9H)
14f-en	197-198	C, 78.41	78.79	3510, 1750, 1690,	1.53(s, 3H), 1.61(s, 3H), 2.28 and 2.75(ABq, J=15Hz, 2H),
		H, 5.92	5.91	1260,	6.13(m, 1H), 7.2-7.7(m, 8H)
18g	186-187	C, 79.22	79.24	2990, 1740, 1680,	1.56(s, 6H), 2.86(s, 2H), 7.4-7.8(m, 4H)
		H, 5.70	5.73	1375, 730	
18h	228-229	C, 85.69	85.60	1740, 1690, 1370,	3.63(s, 2H), 7.0(m, 1H), 7.2-7.5(m, 12H), 7.7(m, 1H)
		H, 4.79	4.74	770, 700	

Table 7   Physical Properties of β-Alkoxy Enone 15

Compound	mp(°C)	Elemental Analysis Calcd.(%) Found(%)		IR(KBr)	^{1}H NMR(CDCl$_3$)
15a	155-156	C, 73.75	73.49	3320, 2960, 1650,	0.82(s, 3H), 1.54(s, 3H), 1.66(s, 3H), 3.96 and 4.56
		H, 6.60	6.55	1635, 1590, 1170,	(ABq, J=7Hz, 2H), 7.3-8.0(m, 4H)
15b	178[a]	C, 76.03	76.22	3340, 2920, 1660,	1.56(s, 3H), 0.9-2.2(m, 10H), 4.55(s, 2H),
		H, 7.09	7.18	1625, 1590, 960	7.2-7.8(m, 4H)
15c-ex	170[a]	C, 73.02	73.14	3260, 2950, 1660,	
		H, 6.13	6.09	1620, 1595, 955	
15c-en		C, 73.02	72.91	3360, 2960, 1665,	0.76(d, J=7Hz, 3H), 1.62(s, 3H), 2.94(m, 1H), 4.16
		H, 6.13	6.15	1625, 1595, 1215	(d, J=8Hz, 1H), 5.00(dd, J=4, 8Hz, 1H), 7.2-7.8(m, 4H)
15d	177-178	C, 72.21	72.26	3350, 1660, 1620,	1.59(s, 3H), 1.93(dd, J=8, 13Hz, 1H), 2.83(dd, J=5, 13Hz,
		H, 5.59	5.57	1595, 1570, 1390	1H), 4.3-5.0(m, 1H), 7.2-7.8(m, 4H)
15g	202.5-203	C, 73.02	73.11	3260, 1640, 1630,	0.98(s, 3H), 1.57(s, 3H), 4.04 and 4.63(ABq, J=7Hz, 2H),
		H, 6.13	6.22	1590, 1170, 1160	5.61(s, 1H), 7.3-8.0(m, 4H)

a, Sublimed.

Table 8   Yields and Physical Properties of 38

Compound	Yield(%)	mp(°C)	Elemental Analysis Calcd.(%) Found(%)		IR(KBr)	^{1}H NMR(CDCl$_3$)[a]
38a 35	78	134-135	C, 71.31	71.59	2960, 1750, 1740	2.12(s, 2H), 7.6-7.8(m, 4H)
			H, 6.34	6.61	1710, 1235	
38b	73	185-186	C, 73.60	73.43	2920, 1755, 1740	1.0-2.1(m, 11H), 2.60(d, J=16Hz, 1H)
			H, 6.79	7.84	1715, 1240	7.4-7.8(m, 4H)
38c-ex	79	162-162.5	C, 70.57	70.80	1760, 1735, 1715	1.9(m, 1H), 2.3(m, 1H), 2.6(m, 1H),
			H, 5.92	5.77	1245	7.5-7.9(m, 4H)
38c-en	84	143-144	C, 70.57	70.67	1750, 1735, 1705	2.0-2.2(m, 2H), 3.3(m, 1H),
			H, 5.92	6.02	1240	7.5-8.0(m, 4H)
38d	63	109-111	C, 69.75	69.55	1760, 1730, 1710	1.7-2.2(m, 4H), 7.3-7.9(m, 4H)
			H, 5.46	5.47	1240	
38e	85	255-257	C, 79.00	78.97	1760, 1745, 1720	2.96 and 3.23(ABq, J=16Hz, 2H),
			H, 5.40	5.56	1235	7.2-7.8(m, 14H)
38f-ex	68	179-180	C, 75.84	75.66	1760, 1750, 1715	2.35 and 3.22(ABq, J-17Hz, 2H),
			H, 5.79	5.76	1240	7.2-7.8(m, 9H)
38f-en	72	214-215	C, 75.84	75.95	1760, 1745, 1715	2.27 and 3.67(ABq, J=16Hz, 2H)
			H, 5.79	5.87	1240	5.9(m, 1H), 7.0-7.8(m, 8H)

a. Data of methyl protons are shown in Figure 5.

Scheme 1

Scheme 2

$$8a, R=CH_3$$
$$8b, R=Ph$$

$$9a, R=CH_3$$
$$9b, R=Ph$$

$$\underset{\sim}{11} \quad 1; \ R^1=R^2=Me$$
$$R^1=Me, \ R^2=CH_2C(Me)_3$$

$$\underset{\sim}{6} \qquad \underset{\sim}{7}$$

(1)
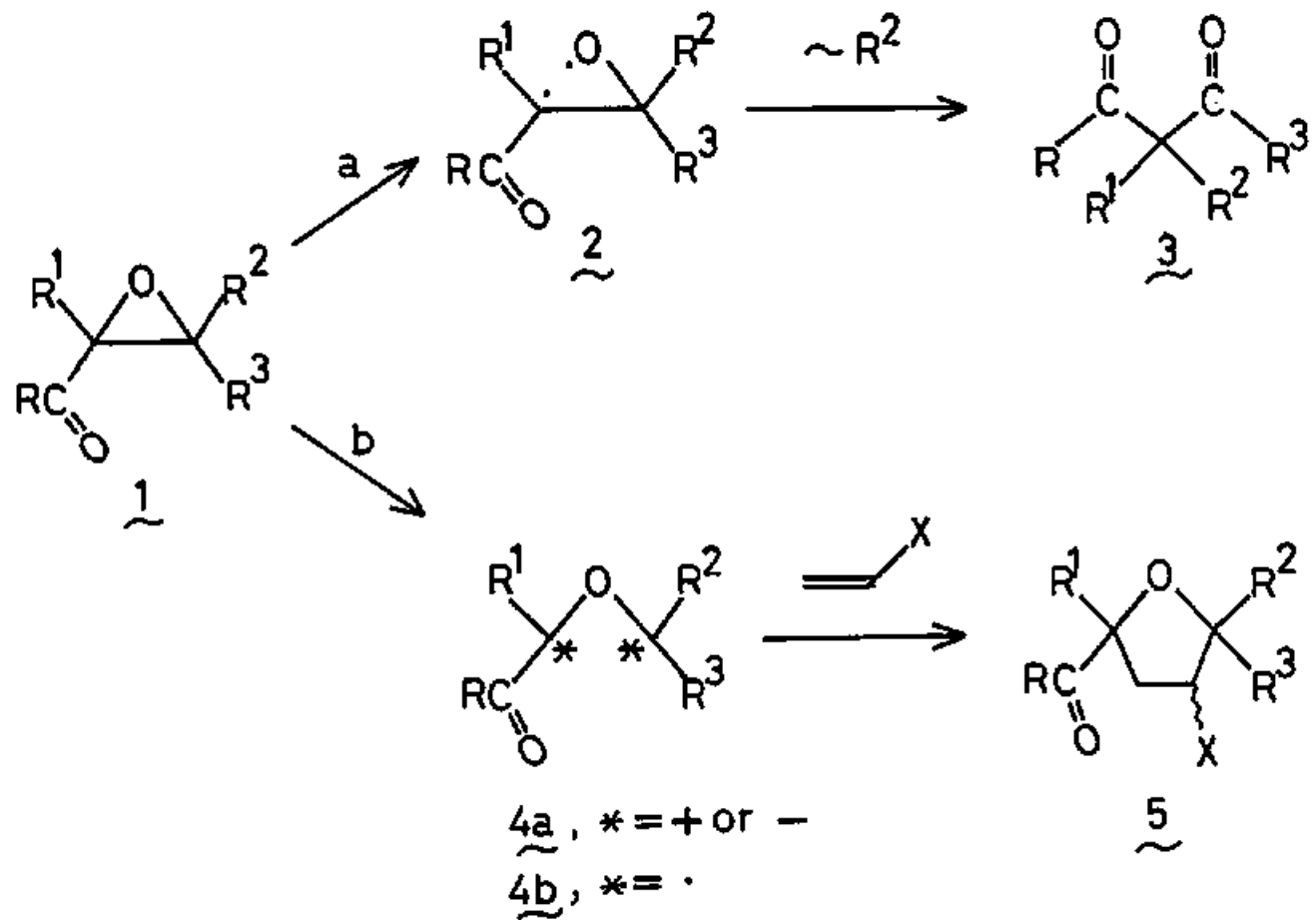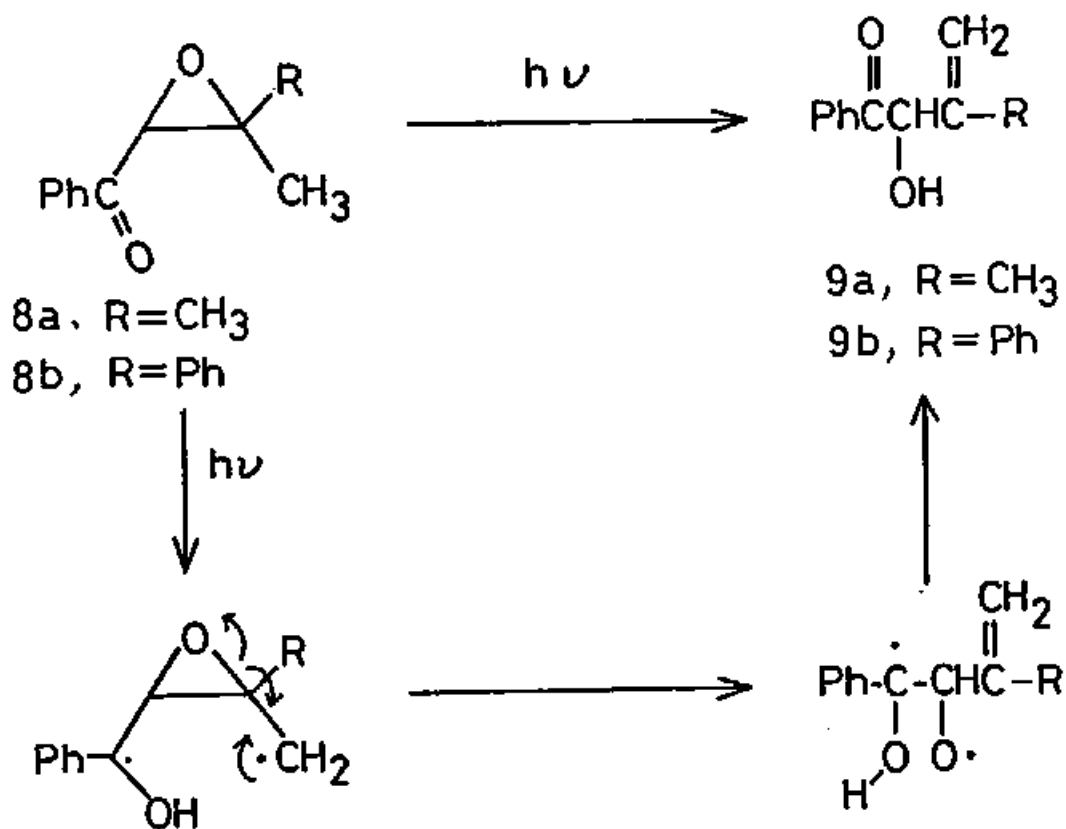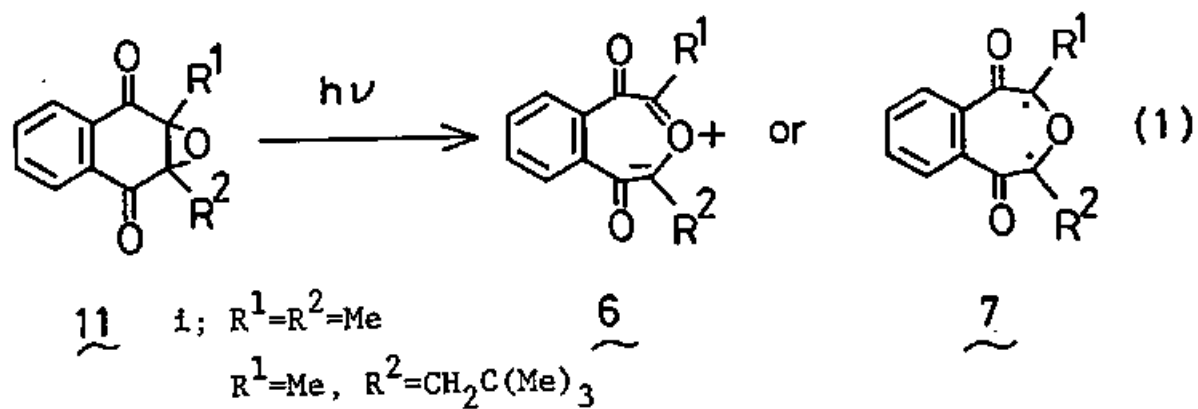
Figure 5. Comparison of the Chemical Shifts of Methyl
Groups of 14 (R=H) with Those of 38 (R=Ac) given in
Parentheses.

1.34(1.48)

a

1.06 (1.26) 1.20(1.38)

1.36(1.50)

b

1.26(1.35)

c-ex

1.30(1.40)

1.33(1.49)

c-en

1.20(1.23)

1.26(1.39)

d

1.36(1.36)

e

1.30(1.55)

f-ex

1.13(1.14)

1.53(1.61)

f-en

1.61(1.65)

11

12

14

15

18
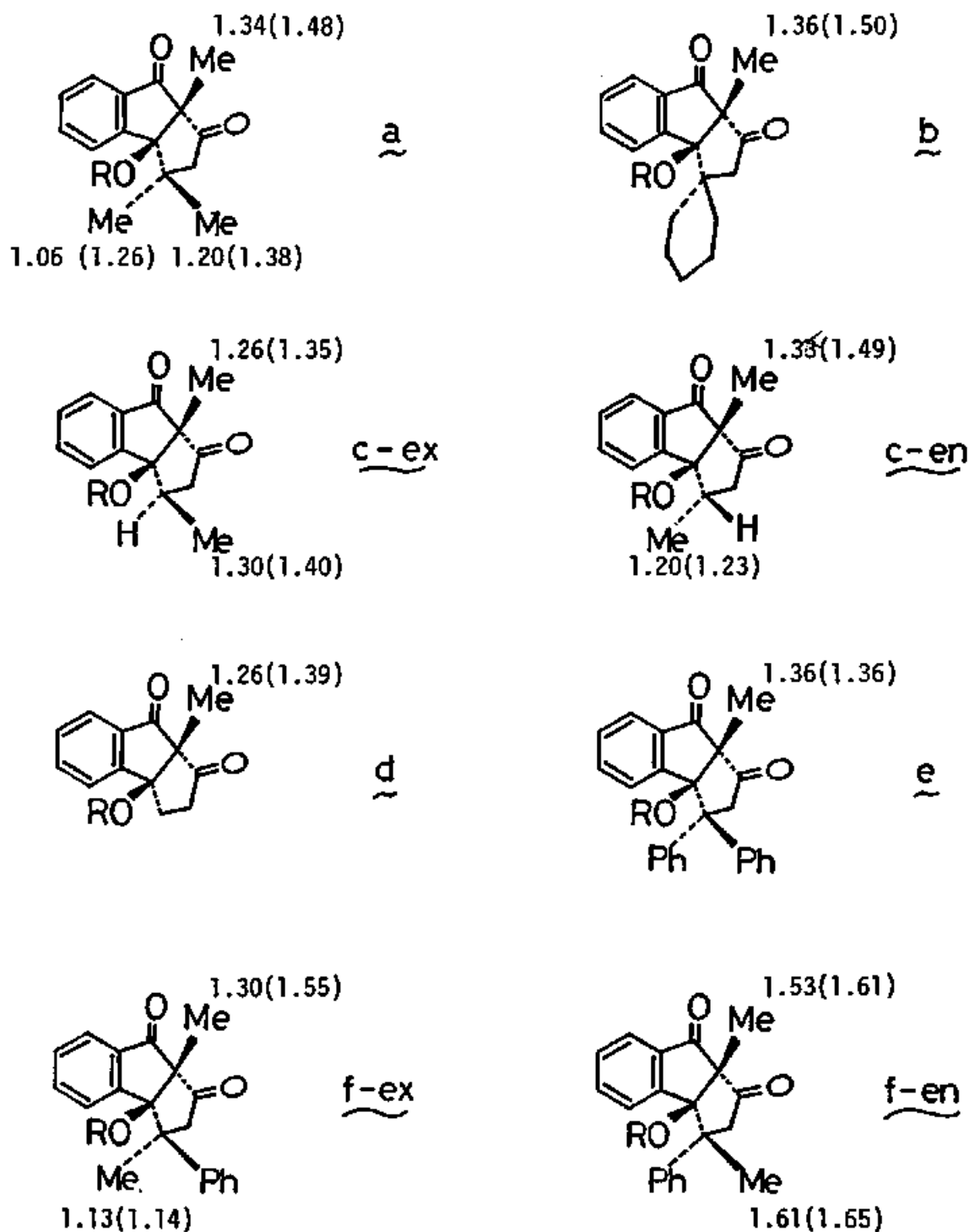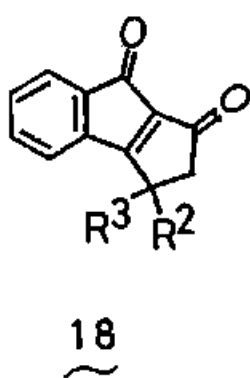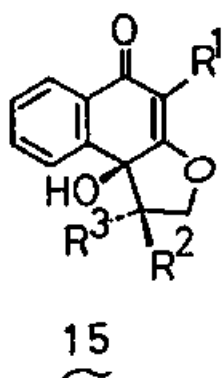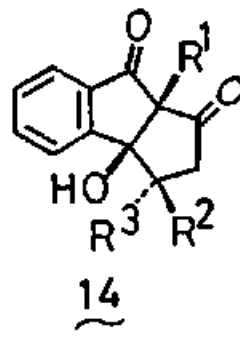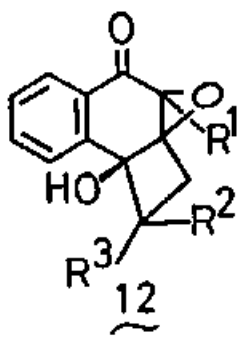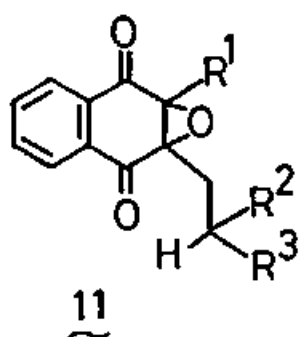
b, R^1=Me, R^2=R^3=Me

c-ex, R^1=R^2=Me, R^3=H

c-en, R^1=R^3=Me, R^2=H

d, R^1=Me, R^2=R^3=H

e, R^1=Me, R^2=R^3=Ph

f-ex, R^1=R^3=Me, R^2=Ph

f-en, R^1=R^2=Me, R^3=Ph

g, R^1=H, R^2=R^3=Me

h, R^1=H, R^2=R^3=Ph

$$\textbf{15} \quad \xrightarrow[\text{Ac}_2\text{O}]{\text{Zn}} \quad \textbf{16} \qquad (3)$$

a, R=CH_3

g, R=H
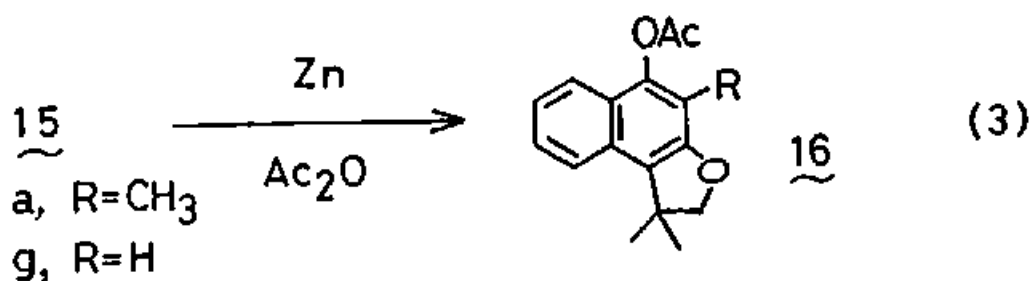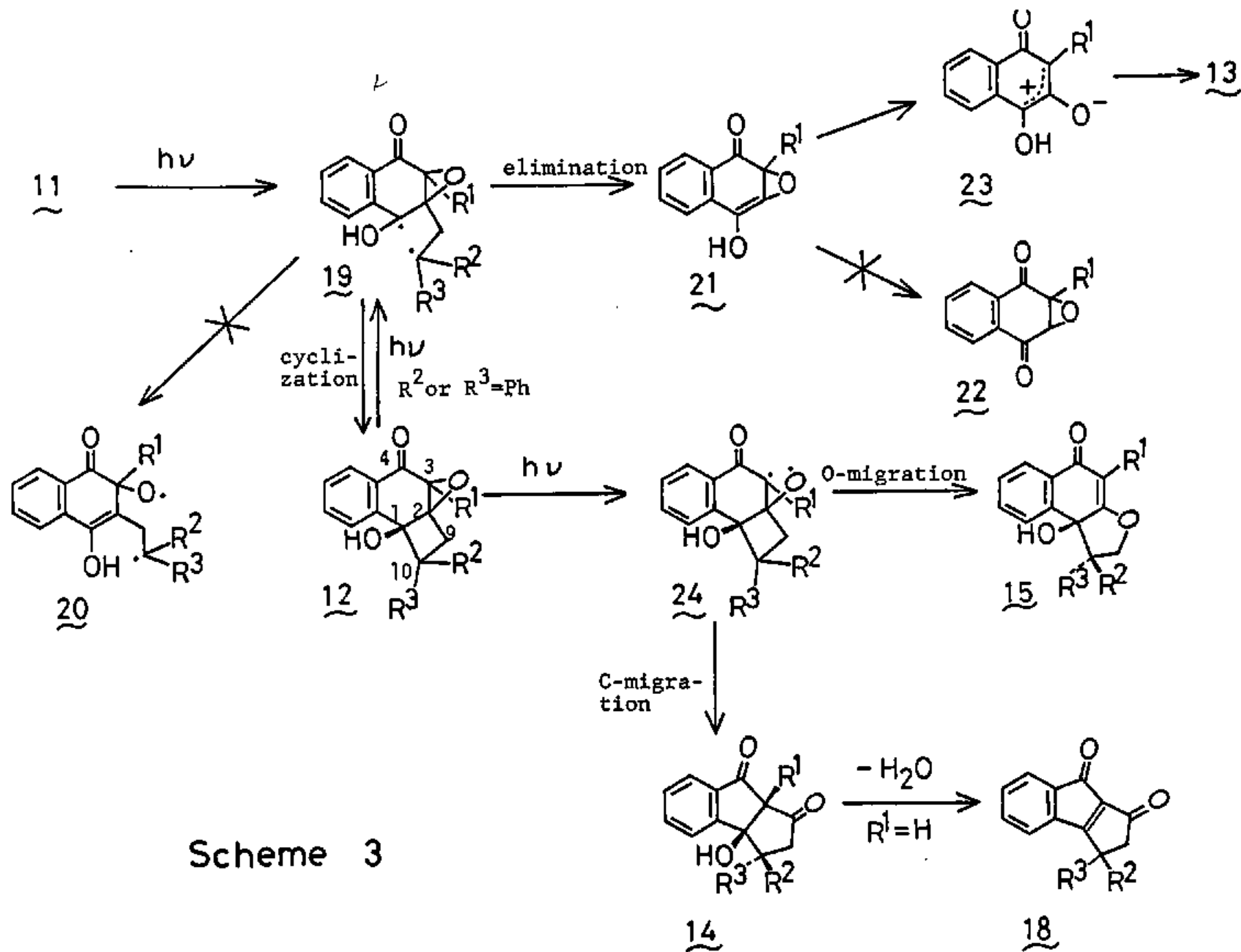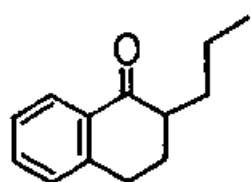
Scheme 3

33
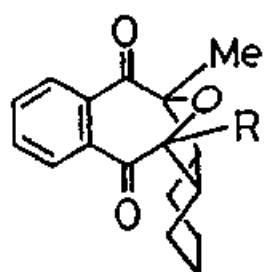
34 i; R=Me
       j; R=CH$_2$C(Me)$_3$

$$ \text{25} \longrightarrow \text{26} \longrightarrow \text{27} \qquad (5) $$

28   **29**

$$ \text{30} \xrightarrow{h\nu} \text{31} \longrightarrow \text{32} \qquad (6) $$

Scheme 4

(7)
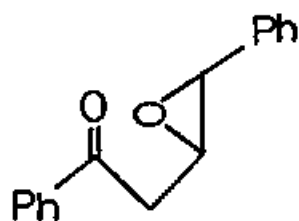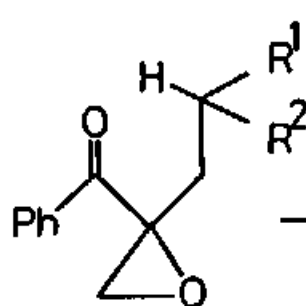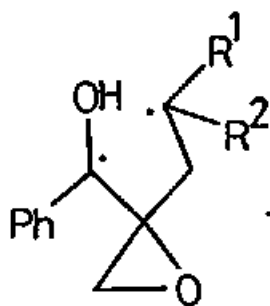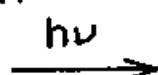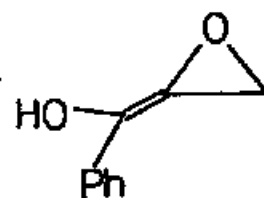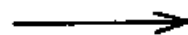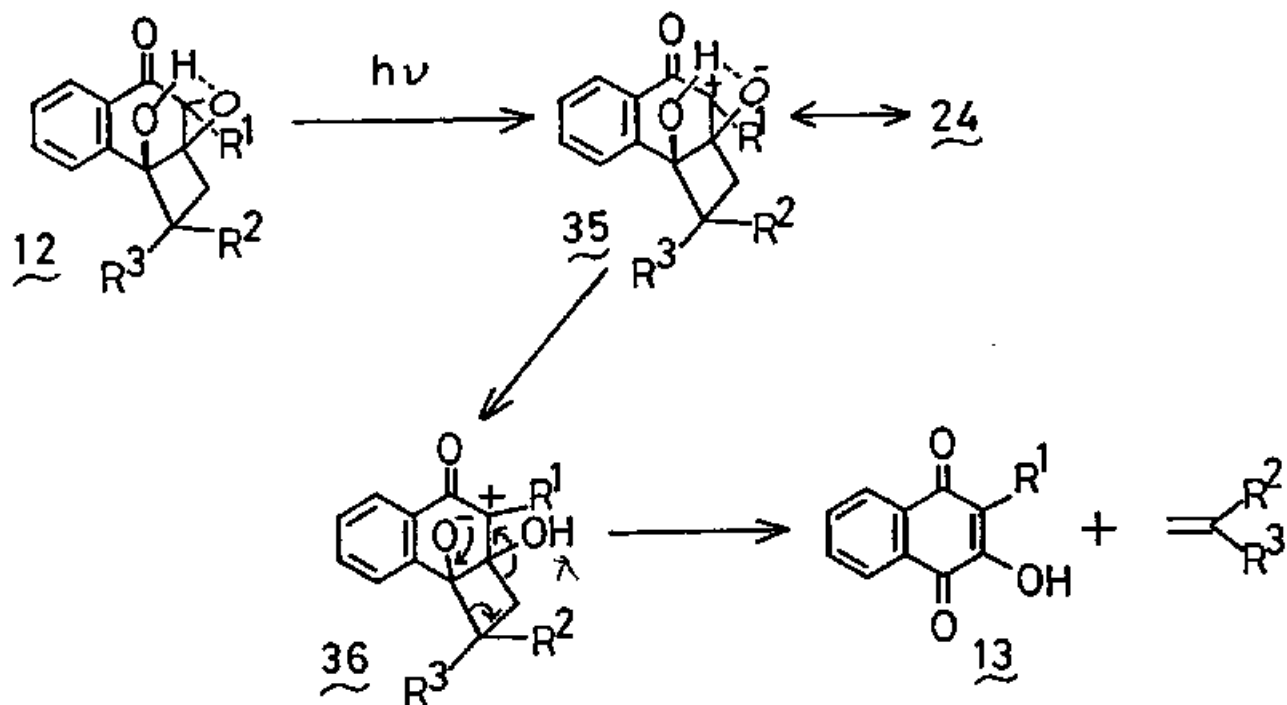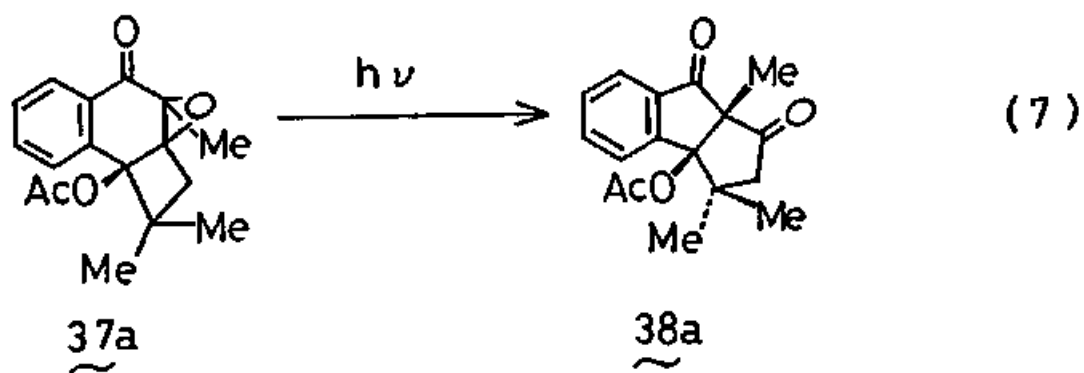
Figure 1. ^{13}C NMR (CDCl$_3$) Data of Selected Photoproducts.

(δ, ppm)

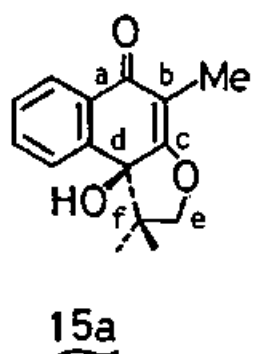

12a
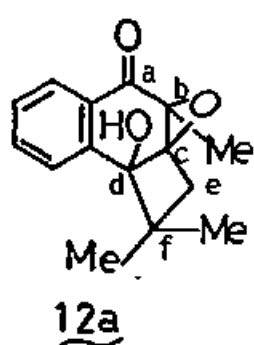
a, 191.9
b, 66.1
c, 59.4
d, 78.1
e, 39.0
f, 40.4

12e
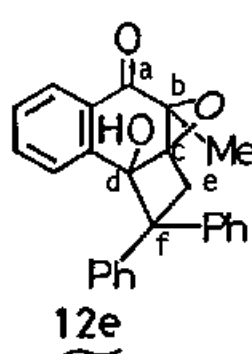
a, 191.4
b, 66.1
c, 59.8
d, 82.1
e, 38.5
f, 59.1

14a
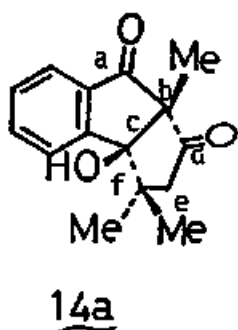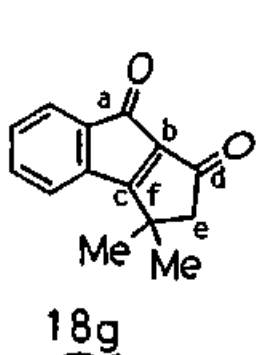
a, 198.8
b, 69.7
c, 87.0
d, 208.3
e, 42.2
f, 52.4

λ

14e
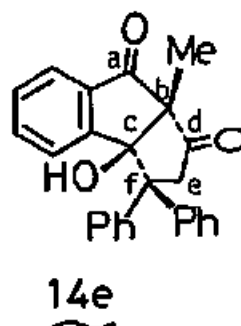
a, 198.0
b, 58.3
c, 89.4
d, 206.5
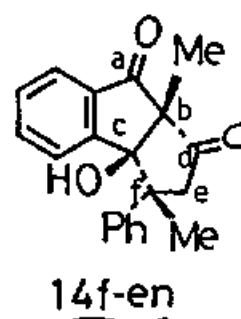e, 49.9
f, 71.1

15a

a, 186.4
b, 109.1
c, 176.6
d, 74.6
e, 83.3
f, 45.2

14f-ex
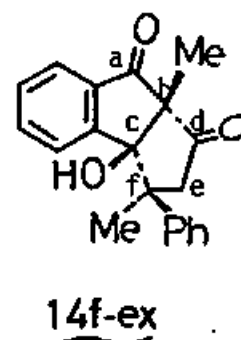
a, 197.7
b, 69.3
c, 86.9
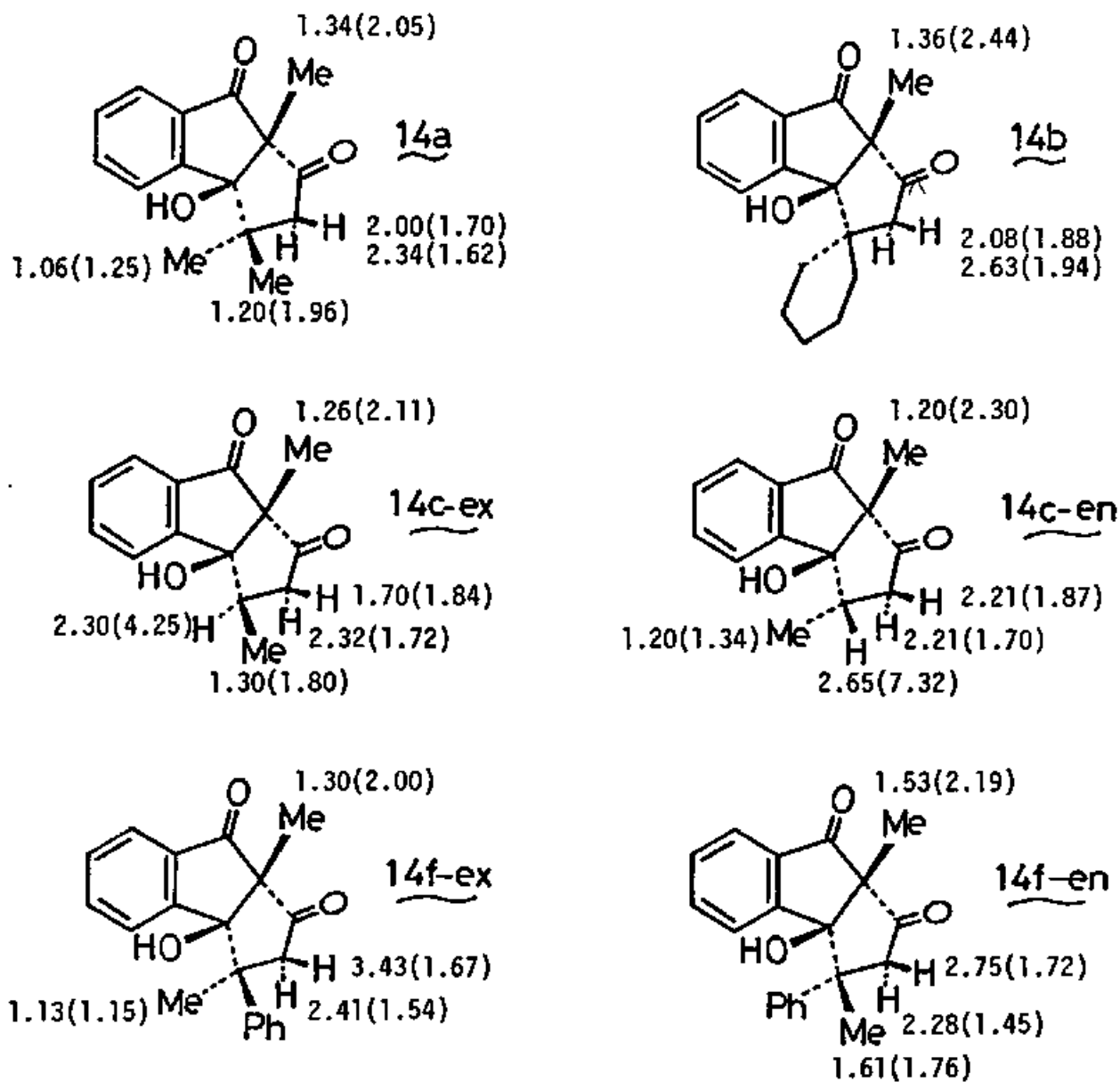d, 208.9
e, 51.0
f, 49.3

18g

a, 195.9
b, –
c, 187.4
d, 203.6
e, 57.5
f, 39.0

14f-en

a, 198.6
b, 70.0
c, 87.3
d, 207.4
e, 48.1
f, 43.9

Figure 2. The ^{1}H NMR Assignments for $\underline{14}$ with Eu(DPM)$_3$ Induced Shifts[a] given in Parentheses.

1.34(2.05)
Me
14a
HO
1.06(1.25) Me
H H
Me
1.20(1.96)
H 2.00(1.70)
2.34(1.62)

1.36(2.44)
Me
14b
HO
H 2.08(1.88)
2.63(1.94)

1.26(2.11)
Me
14c-ex
HO
2.30(4.25)H Me
H H
1.30(1.80)
H 1.70(1.84)
2.32(1.72)

1.20(2.30)
Me
14c-en
HO
1.20(1.34) Me
H H
2.65(7.32)
H 2.21(1.87)
2.21(1.70)

1.30(2.00)
Me
14f-ex
HO
1.13(1.15) Me
H H
Ph
H 3.43(1.67)
2.41(1.54)

1.53(2.19)
Me
14f-en
HO
Ph
Me
1.61(1.76)
H 2.75(1.72)
2.28(1.45)

a) Determined from the plots of shifts (in ppm) *vs.* molar ratio of Eu(DPM)$_3$:$\underline{14}$ by least-squares method; concentrations of $\underline{14}$, *ca.* 0.125 M in CDCl$_3$.
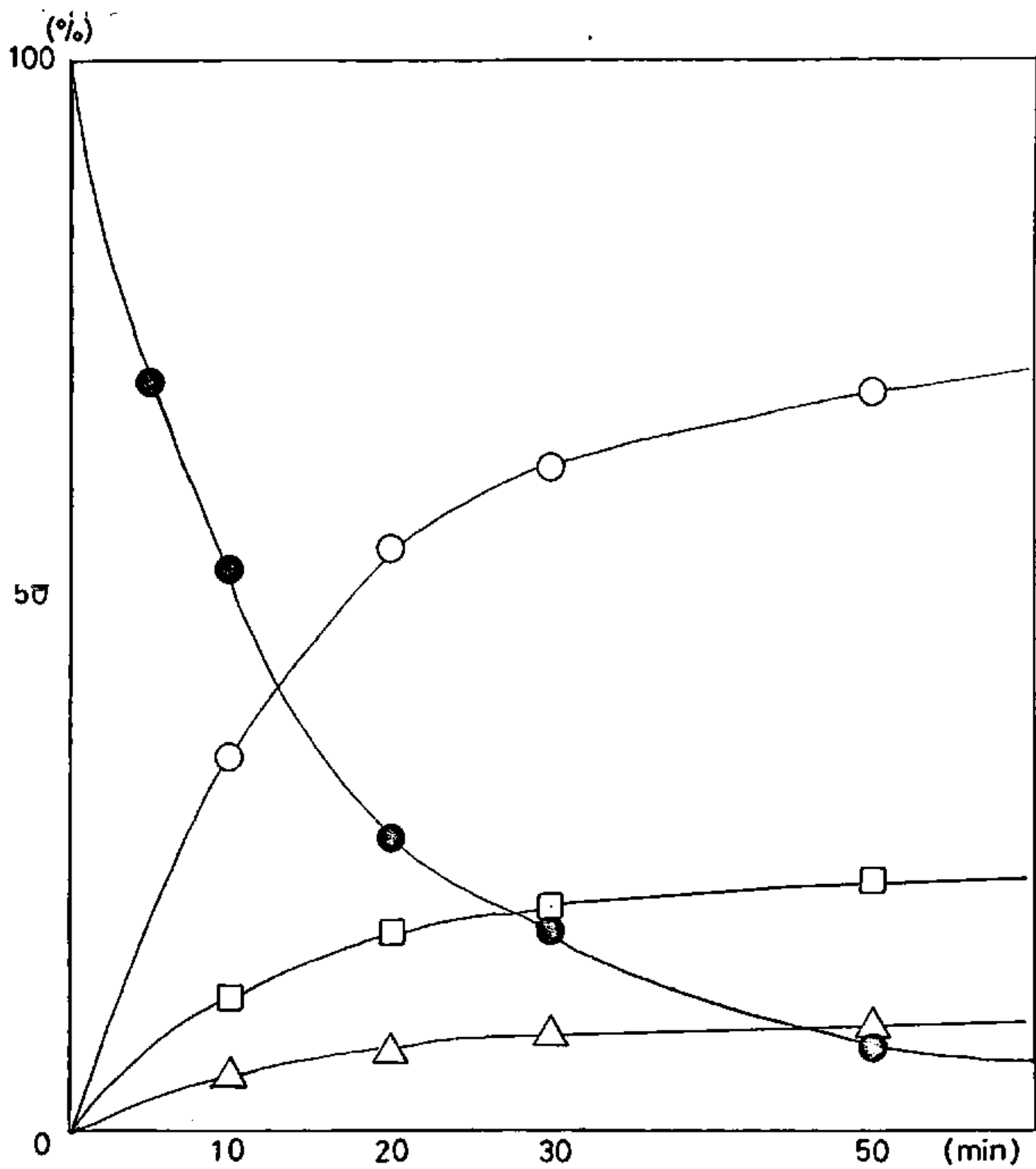
Figure 3.   Photochemical reaction of the cyclobutanol 12a in benzene. Filled symbol ● shows the amount of 12a, while open symbols ○ ,□ , and △ represent the amount of 14a, 15a, and 13a.
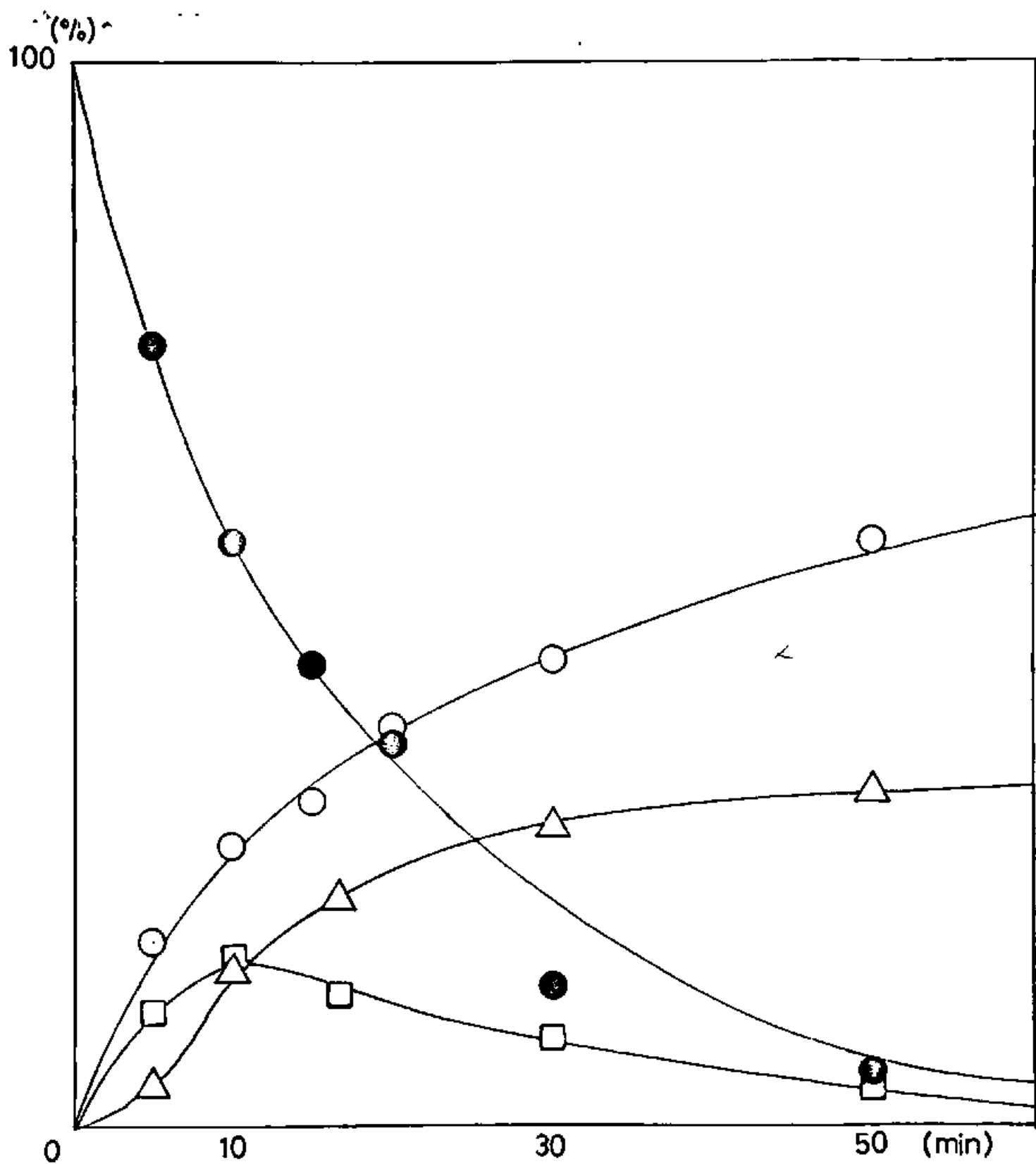
Figure 4.   Photochemical reaction of the cyclobutanol 12e
in benzene. Filled symbol ● shows the amount of 12e, while
open symbols □, ○, and △ represent the amount of 11e,
14e, and 13a.