

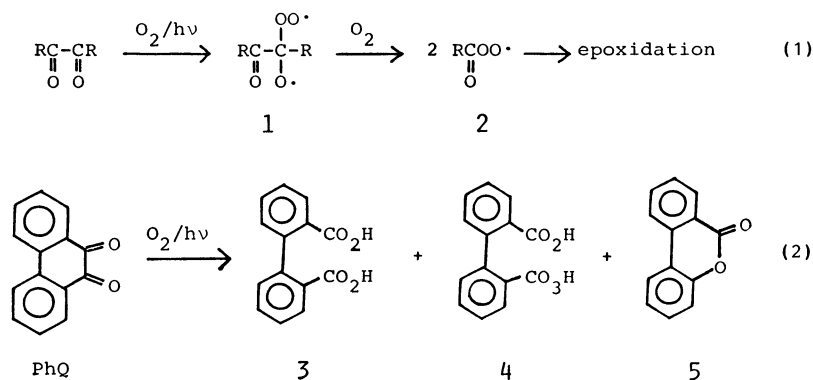


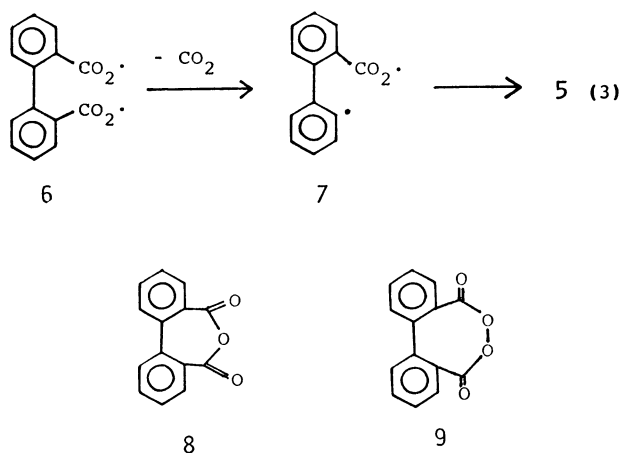
TABLE 1. PHOTOOXIDATION OF PhQ IN BENZENE

Conditions ^{a)}	Rel. Φ ^{b)}	Products (%) ^{c)}					
		3	5	1:1 Adduct ^{d)}	Epoxide	Allylic OOH	Others
	(1.0) ^{e)}	50	1.0				4 (45%)
Air	0.9	45	0.5				4 (40%)
2 mM DABCO	0.03	<1	<1				
0.01 M Cyclohexene	44	28	1.5	50	2	28	
0.1 M Cyclohexene	76	17	1.4	79	11	104	
0.1 M Cyclohexene, N ₂	f	<1	<0.1	89	0	0	
20% THF	98	11	0	80			
0.1 M Cyclooctene	f	9	f	80	6	<1	
0.1 M <i>trans</i> -PhCH=CHMe	f	4	f	82	8	<1	PhCHO (10%), g
0.1 M <i>trans</i> -PhCH=CHPh	f	1	f	90	4	—	PhCHO (13%), h

a) Irradiation of 2.5 mM PhQ through a Pyrex filter for 10–60 min under O₂ at 20 °C unless otherwise noted.

b) Relative quantum yields from the decrease of PhQ as determined by UV absorbance at 420 nm. c) Products were determined by GLC. Allylic hydroperoxide were determined after the reduction with NaBH₄, and the acid after methylation with diazomethane. Peroxy acid 4 was titrated iodometrically. %Yields are based on PhQ.

d) 1:1 Adducts of PhQ with olefins or THF. e) Absolute quantum yield is 0.0048. f) Not determined. g, h) Recovered olefins: *cis/trans*=0.35 and 4, respectively.



detection of diacyl peroxide **9**, we applied the facile reduction of **9** to **8** by triphenylphosphine.^{11a)} Since **9** is known to decompose thermally to afford **5**,^{11b)} some of **5** may be derived from **9**.

The photooxidation of PhQ in the presence of olefin resulted in the sharp decrease in diphenic acid formation and the major reaction changed to the cycloaddition between PhQ and olefins (Table 1). Since the oxygen quenching of triplet ketones is close to the diffusion-controlled rate (*e.g.*, 10⁹ M⁻¹ s⁻¹, 1 M = 1 mol dm⁻³),¹²⁾ it is apparent that the cycloaddition between excited PhQ and olefins is likewise very fast. The photochemical 1,2-cycloaddition (**11**) or 1,4-addition (**10**) of PhQ is well known.¹³⁾ The isomer distributions of these cycloadducts are extensively stud-

ied and shown to change by olefins.¹⁴⁾ The photochemical 1,2-adducts such as **12** are also known for hydrogen donors, *e.g.*, ethers and aldehydes.¹⁵⁾

The epoxide formation was only a minor reaction (2–10%) (Table 1). For cyclohexene, the ratio of epoxide:allylic hydroperoxide was *ca.* 1:10, which was approximately same with the ratio from AIBN-initiated autoxidation at 60 °C.¹⁶⁾ For the case of β -methylstyrene or stilbene, the yield of benzaldehyde, an oxidative C–C cleavage product, was higher than that of epoxides. Thus, it is apparent that the photoepoxidation with PhQ is not effective.

The quantum yield for the photooxidation of PhQ, irradiated at >320 nm in benzene, was $\Phi=0.0048$, which is about one tenth of the benzil case ($\Phi=0.035$).⁷⁾ For comparison, quantum yields were also determined under nitrogen; *i.e.*, $\Phi=0.71$ (lit,^{14a)} 0.79) for the addition of PhQ to 2,3-dimethyl-2-butene and $\Phi=0.95$ (lit,^{15b)} 0.86) for the addition to THF, which are fairly consistent with the literature values as shown. The relative Φ values in Table 1 also suggest that the reaction with olefins or THF is fast and efficient. These will be discussed later.

AcQ. The photooxidation of AcQ gave anhydride **13** as a major product,^{8,15b,17)} 1,8-naphthalene-dicarboxylic acid (**14**) being a minor one (Table 2).

The attempted photoepoxidation with AcQ was not efficient just like the PhQ case. Again, the predominant reaction was the cycloaddition of AcQ to olefins; the 1:1 adducts were a 2,3-dihydro-1,4-dioxin **10** for 1,2-dimethylcyclohexene and 2-acyloxetane **11** for the other olefins (see Experimental for details). The for-

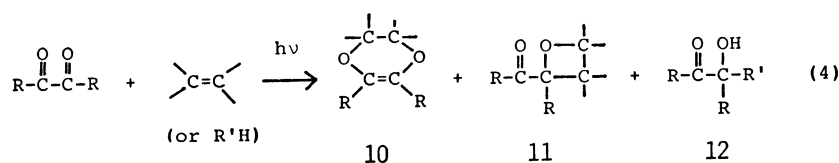
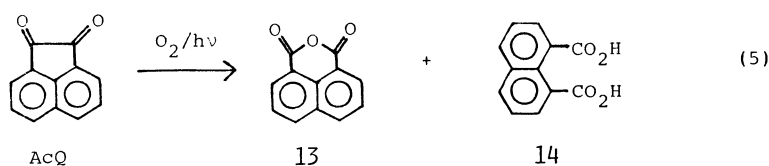


TABLE 2. PHOTOOXIDATION OF AcQ IN DICHLOROMETHANE

Conditions ^{a)}	Rel. Φ ^{b)}	Products (%) ^{c)}					
		Acid 14	Anhydride 13	1:1 Adduct ^{d)}	Epoxide	Allylic OOH	Others
	(1.00) ^{e)}	2.5	79				Peroxy acid (2%)
Air	0.82	3.2	81				
20% THF	1.4	13.5	27	60 ^{f)}			
1 mM DABCO	0.29	1	33	g)			
0.01 M Cyclohexene	2.1	1.5	54	40 ^{h)}	1	12	
0.1 M Cyclohexene	5.2	<1	10	82 ^{h)}	5	70	
0.1 M 1,2-Dimethylcyclohexene	14	<1	1	95 ⁱ⁾	2	30	
0.1 M <i>trans</i> -PhCH=CHMe	5	<1	3	93 ^{j)}	6		PhCHO (12%), ^{k)}
0.005 M <i>trans</i> -PhCH=CHPh	0.5	<1	6	87 ^{j)}	4	—	PhCHO (26%), ^{l)}

a) Irradiation of 10 mM AcQ in CH₂Cl₂ under O₂ at 20 °C through a Pyrex filter for 2.5 h. b) Relative Φ for the decomposition of AcQ (1 mM) as determined by GLC, using a merry-go-round apparatus. c) See footnote c in Table 1. d) 1:1 Adducts of AcQ with olefins or THF. e) Absolute value is 0.0055. f) 1,2-Adduct of THF is reported in Ref. 15b. g) Not determined. h) Oxetane **28**. i) **27**. j) Structures were not determined. k, l) Recovered olefin: *cis/trans*=0.1 and 3.2, respectively.



mation of **10** from AcQ has been reported for 2,3-dimethyl-2-butene;¹⁷⁾ the formations of oxetane **11**^{14c,d)} and α -hydroxy ketone **12**¹⁸⁾ are also known.

Here, some should be noted for the discrepancy between the present results and the reported ones.⁸⁾ The relative quantum yields for the disappearance of AcQ was reported to be almost constant even in the presence of cyclohexene,⁸⁾ which is in sharp contrast to the present results in Table 2. We suppose that since the reported Φ values were determined by monitoring the formation of anhydride **13** by UV, the formation of cycloadduct **11** could not be detected because of the close similarity in UV spectra between AcQ and **11**.

Camphorquinone (CQ). The photooxidation of 2,3-bornanedione (CQ) in benzene was reported to yield many kinds of products involving a rather small amount of camphoric acid (**15**, 7%) and its anhydride (**16**, 3%).¹⁹⁾ The reported yields of **16** change with solvents, *e.g.*, 26% in MeOH,²⁰⁾ 35% in xylene,²¹⁾ and predominant in CCl₄.¹⁹⁾

The attempted photoepoxidation of β -methylstyrene and *trans*-stilbene with CQ resulted in poor yields (5–10%) of epoxide, accompanying C–C cleavage products. Cyclohexene (0.1 M) and CQ afforded 13% epoxide and 68% cyclohexenyl hydroperoxide, indicating again the radical autoxidation of olefin as a major reaction. Like PhQ or AcQ, the photoepoxidation with CQ is not effective.

Comparison of Cyclic and Acyclic α -Diketones.

Quantum yields of the photooxidation in benzene are in the order of biacetyl $\gg$ benzil, CQ $\gg$ AcQ, PhQ, indicating much less effective photolysis for the cyclic diketones. For the photooxidation of benzil and biacetyl there is no accelerating effect by additives such

as olefins, THF or *i*-PrOH; this suggests that the photochemical reactions with these additives are not so fast as those with oxygen. The same is true for cyclic diketone CQ. On the contrary, PhQ reacts very fast with olefins, THF or *i*-PrOH; for example, the photoreaction is 98-fold faster in the presence 20 vol% THF; similar trend is also observed for the case of AcQ (Table 2). As apparent in Tables 1 and 2, the accelerating effect is due to the fast formation of 1:1 adducts; thus, the photoepoxidation with these cyclic diketones is not effective.

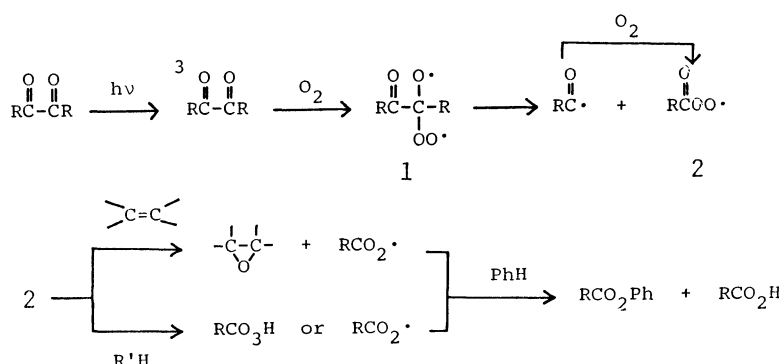
The same features are also shown in the photoepoxidation of stilbene (Table 3). While considerably high yields (50–80%) of epoxide were obtained with benzil and biacetyl, the reaction with cyclic diketones resulted in only 4–7% yields, predominantly affording 1:1 cycloadducts. The photoepoxidation always afforded predominantly *trans*-epoxide (85–95% *trans*), and the *trans* % increases up to over 97% by adding dimethyl sulfoxide (DMSO). Similar effect of DMSO was observed for the coautoxidation of 0.05 M stilbene and 0.2 M benzaldehyde (initiated by α,α' -azobisisobutyronitrile at 60 °C); % *trans* increased from 65% to 98% by adding DMSO. It is well known that the coautoxidation of aldehyde and olefin affords a mixture of *cis*- and *trans*-epoxides, the epoxidizing species being acylperoxyl radical and peroxy acid.²²⁾ These results suggest that the peroxy acid epoxidation is effectively reduced by DMSO²³⁾ and the epoxidation by acylperoxyl radical proceeds with high selectivity (*i.e.*, >98%) for *trans*-stilbene oxide.

Here, some should be noted about the quenching by DABCO (1,4-diazabicyclo[2.2.2]octane). The results in Tables 1 and 2 show an effective quenching by DABCO for the diketone photooxidation.²⁴⁾ However,

TABLE 3. PHOTOEPOXIDATION OF STILBENE WITH α -DIKETONES UNDER O_2

Diketone	Solvent(additive) ^{b)}	Products (%) ^{a)}		Major reaction
		PhCHO	Epoxide(cis: trans)	
A) Photoepoxidation of <i>trans</i> -stilbene ^{c)}				
Benzil	PhH	20	62 (7:93) ^{d)}	Epoxidn.
	PhH (DMSO)	18	51 (2:98) ^{d)}	Epoxidn.
PhQ	CH ₂ Cl ₂	22	4 (5:95)	1:1 Adduct ^{e)}
	CH ₂ Cl ₂ (DMSO)	16	5 (3:97)	1:1 Adduct ^{e)}
AcQ	CH ₂ Cl ₂	8	7 (15:85)	1:1 Adduct ^{e)}
	CH ₂ Cl ₂ (DMSO)	f)	4 (5:95)	1:1 Adduct ^{e)}
CQ	PhH (DMSO)	4	6 (3:97)	g)
B) Coautoxidation with PhCHO-AIBN ^{b)}				
<i>trans</i> -Stilbene	PhH	f)	(0:100)	Epoxidn.
<i>cis</i> -Stilbene	PhH	f)	(35:65)	Epoxidn.
<i>cis</i> -Stilbene	PhH (DMSO)	f)	(2:98)	Epoxidn.

a) Products were determined by GLC based on the consumed diketone. b) 0.1 M DMSO was added. c) Irradiation of 2 mM diketone and 0.05 M *trans*-stilbene solution through a Pyrex filter under O_2 (20 °C, 2 h). Recovered olefin: cis/trans=4–9. d) The cis/trans ratios were practically the same when *cis*-stilbene was used. e) 1:1 Adducts of diketone and olefin. See Tables 1 and 2. f) Not determined. g) Many products were detected by GLC, but not identified. h) Coautoxidation of 0.05 M stilbene and 0.2 M benzaldehyde was initiated by the thermal decomposition of AIBN (≈ 5 mM) at 60 °C.



Scheme 1.

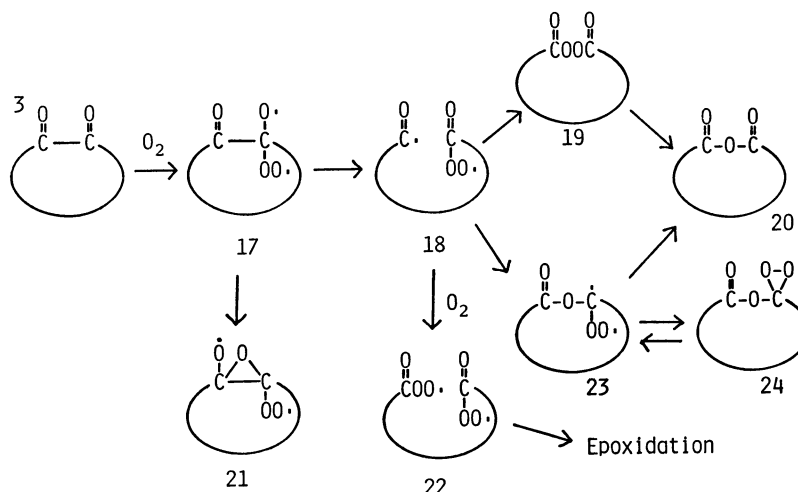
the apparent quenching by DABCO does not mean that the diketone photooxidation proceeds *via* a singlet oxygen reaction, since the photolysis of benzil was rather retarded by adding Methylene Blue or Rose Bengal, an efficient 1O_2 sensitizer. The addition of DABCO to PhQ in benzene resulted in weakly reddish solution with a few percent increase in the absorbance at >300 nm. Probably this indicates the formation of a C–T complex between PhQ and DABCO, which may act as an efficient energy acceptor for the excited PhQ*, quenching the PhQ photolysis. This was ascertained by the fact that the cycloaddition of PhQ with cyclohexene is also efficiently quenched by DABCO. The same is probably true for the other diketones in Table 3, although no absorption due to C–T complex could be detected by UV.

Mechanism. The photoepoxidation of acyclic α -diketones has been shown to proceed by way of Scheme 1.⁷⁾ A considerable amount of phenyl benzoate was obtained for the benzil photooxidation in benzene (*i.e.*, R=Ph).⁷⁾

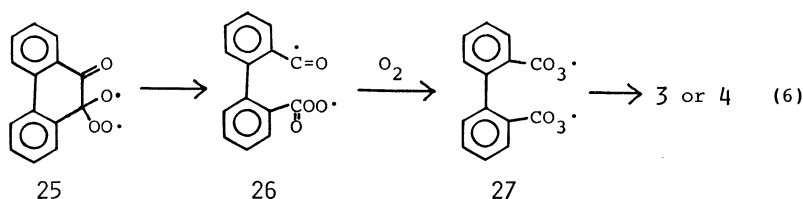
The photooxidation of AcQ affords anhydride as a major product. Similar anhydride formations are

also known for the photooxidation of CQ^{19–21)} and other cyclic diketones.^{20,25)} Some possible routes for the formation of anhydride (**20**) from cyclic diketones may be written as Scheme 2. This mechanism is, in parts, similar to that reported by Koo and Schuster,⁸⁾ but essentially different in the fate of alkoxy radical **17**. The β -scission of alkoxy radical **17** to afford **18** is probably facile since the scission of acyl radical in α -acylalkoxy radicals has been established to be very fast.²⁶⁾ The conversion of **17** to **21**, as was suggested,⁸⁾ seems to be unfavorable on the basis of an energetic point of view that **21**, an oxirane diradical, would be much less stable than **17**, a ketone diradical. No formation of anhydride from PhQ also supports the pathway **17**→**18**.

The next choice is about the reactions of radical pair **18**. It seems to couple easily to diacyl peroxide **19**, but, **19** is not likely to afford smoothly anhydride **20**.²⁷⁾ An alternative reaction of **18** is the intramolecular addition of acyl radical to carbonyl oxygen to afford **23**. Since the addition of acyl radical to carbonyls is known intermolecularly,²⁹⁾ the intramolecular addition (*i.e.*, **18**→**23**) may proceed smoothly.



Scheme 2.



It is not certain that intermediate diradical **23** might be equilibrated with unstable dioxirane (**24**) or not. These unstable intermediate **23** and **24** are probably a poor O-transfer agent to olefins.³⁰⁾ In the photooxidation of AcQ the formation of only small amount of diacid **14** indicates that intramolecular addition of acyl radical **18** to form **23** is much faster than the trapping by oxygen to afford **22** (*i.e.*, ultimately **14**). The anhydride formation in benzene is only 3% from CQ¹⁹⁾ and <1% from PhQ, suggesting that the anhydride formation from α -diketones is not a general or primary photochemical event.

In the photooxidation of PQ the predominant formation of diphenic acid (**3**) and peroxy acid (**4**) suggests that, after fast C–C scission in **25**, the resulting diradical **26** is effectively trapped by oxygen (Eq. 6). In other words, an intramolecular cyclization of **26** to **9** or to diradical **23** is much slower than the trapping of acyl radical **26** by oxygen. One reason for the unfavorable intramolecular coupling of **26** (or **18**) may be the free rotation of two aryl rings in **26**, which is not the case for AcQ or CQ of fixed carbon skeleton. Another reason is probably due to spin multiplicity effect.³¹⁾ There are many cases where coupling products from triplet radical pairs are of much lower yields than those of corresponding singlet ones.³²⁾ The present reaction of triplet quinones with oxygen would produce predominantly triplet or quintet diradical **25** and hence **26**.³³⁾ Thus the ring closure of **26** to **9** becomes less efficient as observed.

In conclusion, the photooxidation of PhQ proceeds *via* the similar pathway (*i.e.*, **17**→**18**→**22**) as is the case for acyclic benzil, while AcQ gives anhydride probably by way of **17**→**18**→**23**→**20**. The photoepoxidation with cyclic α -diketones is not efficient, 1:1

cycloadditions being predominant. The epoxidation as a minor reaction affords chiefly *trans*-epoxide accompanying a significant amount of C–C cleavage products. The addition of DMSO results in much higher selectivity for *trans*-epoxide. These facts suggest that the photoepoxidation with cyclic α -diketones proceeds by way of acylperoxyl radical just as acyclic ones.

Experimental

Melting points were measured by a Yanagimoto micro melting point apparatus and are corrected. ¹H NMR spectra were recorded with a Hitachi R24-B spectrometer, IR spectra with a Perkin-Elmer 337 spectrometer, and UV with a Hitachi 124 spectrophotometer. GLC analysis were performed with a Yanagimoto G 180 gas chromatograph using two different 1 m columns: PEG 20M, 20% on Chamelite CK; Silicon OV-17, 5% on Shimalite W.

Materials. AcQ and PhQ were prepared according to literatures, mp 260 °C (lit.³⁴⁾ 259–260 °C) and 205–208 °C (lit.³⁵⁾ 209–210 °C), respectively. CQ was obtained by selenium dioxide oxidation of camphor in AcOH (reflux, 2 h), mp 198–199 °C (lit.³⁶⁾ 198 °C). *cis*-Stilbene (95% pure) was obtained by benzil-sensitized photoisomerization of *trans*-stilbene. Other olefins were of commercial sources.

Photooxidation of PhQ. A typical procedure is as follows. A 5 ml benzene solution of 2.5 mM PhQ was irradiated under oxygen through a Pyrex filter using a medium pressure 300 W Hg lamp at *ca.* 20 °C. Products were determined by GLC directly and carboxylic acids were analyzed after methylation with diazomethane. Peroxy acid was titrated as described previously.³⁷⁾ A small amount of 2,2'-biphenylcarbolactone **5** was detected by GLC, but diphenic anhydride was not. Diphenic acid was identified as dimethyl ester and also by the thermal conversion to diphenic anhydride.

The photoepoxidation of olefins with diketone was conducted similarly and resulting allylic hydroperoxides were determined after the reduction with NaBH_4 and MeOH . The results are listed in Table 1. Since the cycloaddition of PhQ with olefins has extensively studied,^{13,14} the 1:1 adducts were not isolated.

Quantum yields for the photooxidation of PhQ were determined using trioxalatoferrate(III) actinometry³⁸) and/or a merry-go-round apparatus.

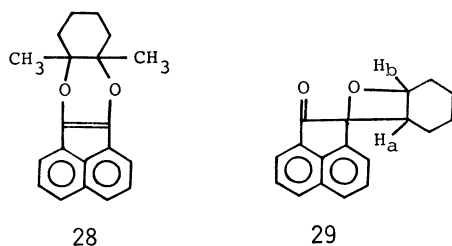
Photooxidation of AcQ. The photooxidation of AcQ was carried out similarly with the PhQ case. The GLC analysis showed a predominant formation of anhydride **13** together with a minor amount of diacid (**14**).

The photoepoxidation of olefins with AcQ were conducted similarly and the results are shown in Table 2. As exemplified below, the major photochemical reaction of AcQ with olefins is 1,2- or 1,4-cycloaddition to yield oxetanes (**11**) or **10**.

Photoreaction of AcQ with 1,2-Dimethylcyclohexene. A CH_2Cl_2 solution (20 ml) of AcQ (60 mg) and 1,2-dimethylcyclohexene (0.15 ml) was irradiated under air for 5 h. The NMR spectra of the crude reaction mixture indicated a single reaction product. Purification by passing through a Florisil column (20 g) using hexane- CH_2Cl_2 (9:1) afforded red dihydrodioxin **28** in ca. 60% yield, mp 134–136 °C. NMR (δ , CCl_4): 1.5–1.8 (m, 8H, methylenes), 1.39 (s, 6H, two methyl), and 7.2–7.5 (m, 6H, aromatic protons); UV (hexane): 465 and 485 (ϵ 520), 316 (5100), 303 (5700), and 228 nm (22000).

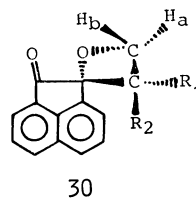
Found: C, 82.26; H, 7.33; O, 10.41%. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2$: C, 82.15; H, 6.89; 10.95%.

The NMR and UV spectra are close to those of the corresponding dihydroxin from AcQ and 2,3-dimethyl-2-butene; NMR (δ), 1.37 and 7.2–7.5; UV, 450, 318, 306, and 230 nm.¹⁷)



Photoreaction of AcQ with Cyclohexene. A similar reaction of AcQ with cyclohexene under air and column chromatography using hexane- CH_2Cl_2 (1:1) gave oxetane **29** in 65% yield. NMR spectra (δ , CDCl_3), 1.2–2.2 (m, 8H, methylenes), 3.10 (q, $J=20$ Hz, H_a), 5.5–5.8 (m, H_b) and 7.5–8.2 (m, 6H, aromatic protons); UV (hexane), 338 (ϵ 3300), 325 (sh, 3600), 310 (4420), 300 (sh, 3800), 277 (2700), and 223 nm (3600).

Photoreaction of AcQ with 1,1-Diphenylethylene. The 5 h irradiation of AcQ (60 mg) and olefin (120 mg) in CH_2Cl_2 (20 ml) under air yielded a single product as checked by NMR. Purification by passing through a Florisil column using CH_2Cl_2 and recrystallization from hexane- CH_2Cl_2 gave pure crystals of oxetane **30a** in 19% yield, mp 220–224 °C (decomp). NMR spectra (δ , CDCl_3), 5.53 (d, $J=6$ Hz, H_a), 6.10 (d, $J=6$ Hz, H_b) and 6.5–8.1 (m, 16H aromatic protons). IR (Nujol), 1730 cm^{-1} (C=O); UV (hexane), 342 (ϵ 3000), 325 (sh, 2780), 313 (3620), 300 (sh, 2850), 284 (sh, 3140), 254 (sh, 6750), and 223 nm (16000). The structure **30a** as shown was deduced from the NMR spectra in comparison to corresponding protons in oxetanes.³⁹)



- | | |
|---|--|
| a | $\text{R}_1 = \text{R}_2 = \text{Ph}$ |
| b | $\text{R}_1 = \text{Me}, \text{R}_2 = \text{Ph}$ |
| c | $\text{R}_1 = \text{Ph}, \text{R}_2 = \text{Me}$ |

Photoreaction of AcQ with α -Methylstyrene. The irradiation of CH_2Cl_2 solution (25 ml) of AcQ (60 mg) and α -methylstyrene (0.3 ml) under air afforded 1:1 mixture of two oxetane isomers in the combined yield of over 90% as determined by NMR. The two isomers were separated by passing a Florisil column (50 ml) using hexane- CH_2Cl_2 (1:1). The earlier fractions gave 4 mg (6%) of pure oxetane **30b**, mp 102–108 °C; NMR (δ , CCl_4), 1.71 (s, 3H, CH_3), 4.93 (d, $J=6$ Hz, 1H, H_a), 5.38 (d, $J=6$ Hz, 1H, H_b) and 6.4–8.0 (m, 11H, aromatic protons).

The latter fractions, after the recrystallization from hexane- CH_2Cl_2 , afforded pure oxetane **30c** in 6% yield, mp 161–161.5 °C; NMR (δ , CCl_4), 1.82 (s, 3H, CH_3), 4.40 (d, $J=5$ Hz, 1H, H_a), 5.82 (d, $J=5$ Hz, 1H, H_b) and 6.4–8.0 (m, 11H, aromatic protons). UV spectra in hexane are the same for **30b** and **30c**; 337 (ϵ 3020), 326 (sh, 2940), 312 (4140), 300 (3560), 284 (sh, 3200), 260 (sh, 5750), 252 (6680), and 223 nm (27000). IR (film): 1730 cm^{-1} (C=O).

Found: C, 88.88; H, 5.71%. Calcd for $\text{C}_{21}\text{H}_{16}\text{O}$: C, 88.98; H, 5.37%.

References

- 1) M. Koizumi, S. Kato, N. Mataga, and T. Matsuura, "Photosensitized Reactions," Kagakudozin, Kyoto (1978).
- 2) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968); K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).
- 3) P. D. Bartlett, *Chem. Soc. Rev.*, **1976**, 149; P. D. Bartlett, "Organic Free Radicals," ed by W. A. Pryor, Am. Chem. Soc., Washington D. C. (1978), p. 15; P. D. Bartlett and H. S. Ho, *J. Am. Chem. Soc.*, **96**, 627 (1974); C. W. Jefford and A. F. Boshung, *Helv. Chim. Acta*, **57**, 2257 (1974); P. D. Bartlett and M. E. Landies, *J. Am. Chem. Soc.*, **99**, 3033 (1979).
- 4) a) N. Shimizu and P. D. Bartlett, *J. Am. Chem. Soc.*, **98**, 4193 (1976); b) P. D. Bartlett and J. Becherer, *Tetrahedron Lett.*, **1978**, 2983; c) P. D. Bartlett, A. A. M. Roof, and N. Shimizu, *J. Am. Chem. Soc.*, **104**, 3130 (1982).
- 5) J. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977); J. Eriksen and C. S. Foote, *ibid.*, **102**, 6083 (1980).
- 6) H. S. Ryang and S. Y. Wang, *J. Am. Chem. Soc.*, **100**, 1302 (1978); M. Malacria and J. Goré, *J. Org. Chem.*, **44**, 885 (1979); G. Buchi, K. W. Fowler, and A. M. Nadzam, *J. Am. Chem. Soc.*, **104**, 544 (1982).
- 7) Y. Sawaki and C. S. Foote, submitted for publication.
- 8) J. Y. Koo and G. B. Shuster, *J. Org. Chem.*, **44**, 847 (1979).
- 9) Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, **103**, 2049 (1981).
- 10) J. Saltiel and H. C. Curtis, *Mol. Photochem.*, **1**, 239 (1969).
- 11) a) F. Ramirez, N. B. Desai, and R. B. Mitra, *J. Am. Chem. Soc.*, **83**, 492 (1961); b) J. Y. Koo and G. B. Schuster, *ibid.*, **99**, 6107 (1977).
- 12) N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings, Menlo Park, Calif., (1978), pp. 354 and 589; Ref. 1, p. 220.

- 13) a) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York (1968), p. 119; b) G. P. Fundt and G. O. Schenck, "1,4-Cycloadditions," ed by J. Hamer, Academic Press, New York (1967), p. 345.
- 14) a) S. Farid and K. H. Scholz, *Chem. Commun.*, **1968**, 412; b) Y. L. Chow, J. C. Joseph, H. H. Quon, and J. N. S. Tam, *Can. J. Chem.*, **48**, 3045 (1970); c) T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *J. Am. Chem. Soc.*, **99**, 871 (1977); d) K. Maruyama, T. Iwai, Y. Naruta, T. Otsuki, and Y. Miyagi, *Bull. Chem. Soc. Jpn.*, **51**, 2052 (1978).
- 15) a) Ref. 13a, chaps. 18 and 19; b) K. Maruyama, K. Ohno, and J. Osugi, *Bull. Chem. Soc. Jpn.*, **45**, 847 (1972).
- 16) Y. Sawaki, unpublished results.
- 17) T. S. Fang and L. A. Singer, *J. Am. Chem. Soc.*, **100**, 6278 (1978).
- 18) H. Takeshita, A. Mori, M. Funakura, and H. Mametzuka, *Bull. Chem. Soc. Jpn.*, **50**, 315 (1977).
- 19) J. Meinwald and H. O. Klingele, *J. Am. Chem. Soc.*, **88**, 2071 (1966).
- 20) G. E. Gream, J. C. Paice, and C. C. R. Ramsay, *Aust. J. Chem.*, **22**, 1229 (1969).
- 21) M. B. Rubin and R. G. La Barge, *J. Org. Chem.*, **31**, 3283 (1966).
- 22) F. Tsuchiya and T. Ikawa, *Can. J. Chem.*, **47**, 3191 (1969); R. R. Diaz, K. Selby, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 360.
- 23) The peroxy acid oxidation of DMSO is *ca.* 1000-fold faster than that of styrene.⁹⁾
- 24) The strong irradiation (500 W lamp) of 0.05 M benzil was not effectively quenched by 5 mM DABCO.⁷⁾ We suppose that the relatively small amount of DABCO might be oxidized by peroxy acid produced.
- 25) J. Rigaudy, and N. Paillous, *Tetrahedron Lett.*, **1966**, 4825; C. W. Bird, *Chem. Commun.*, **1968**, 1537.
- 26) Y. Sawaki and Y. Ogata, *J. Org. Chem.*, **41**, 2340 (1976).
- 27) It is not facile to convert diacyl peroxides to anhydrides in the absence of deoxygenating agents such as phosphines. Only one exception is the reported reaction of diacyl peroxides with aliphatic olefins to yield anhydrides and epoxides.²⁸⁾ The present anhydride formation from AcQ, however, does occur smoothly only in the absence of olefins, thus denying the anhydride formation *via* **19**.
- 28) F. D. Greene and W. Adam, *J. Org. Chem.*, **29**, 136 (1964).
- 29) C. Walling, "Free Radicals in Solution," Wiley, New York (1957), p. 282; W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964); W. H. Urry, A. Nishihara, and J. H. Niu, *ibid.*, **32**, 347 (1967); D. L. Bunbury and T. T. Chuang, *Can. J. Chem.*, **47**, 2045 (1969).
- 30) For reactivities of carbonyl oxides, see Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, **103**, 3832 (1981).
- 31) T. Koenig and H. Fisher, "Free Radicals," ed by J. K. Kochi, Wiley, New York (1973), Vol. I, p. 179.
- 32) For example, J. R. Fox and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4031 (1964); T. Nakata, K. Tokumaru, and O. Shimamura, *Tetrahedron Lett.*, **1967**, 3303; P. R. Story, W. H. Morrison, III, and J. M. Butler, *J. Am. Chem. Soc.*, **91**, 2398 (1969).
- 33) Ref. 1, p. 218.
- 34) C. F. M. Allen, J. A. Van Allan, *Org. Synth.*, Coll. Vol. III, p. 1 (1955).
- 35) S. Kato, M. Maezawa, and J. Hashimoto, *Yuki Gosei Kagaku Kyokai Shi*, **15**, 402 (1957).
- 36) J. Lifschitz, *Zeit. Phys. Chem.*, **105**, 27 (1923).
- 37) Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, **98**, 7324 (1976).
- 38) J. G. Calvert, J. N. Pitts, Jr., "Photochemistry," Wiley, New York (1966), p. 783.
- 39) See for example, Ref. 4a; N. Shimizu, *J. Am. Chem. Soc.*, **96**, 6456 (1974).