Photooxidation of Olefins Sensitized by α-Diketones and by Benzophenone. A Practical Epoxidation Method with Biacetyl

Nobujiro Shimizu and Paul D. Bartlett*

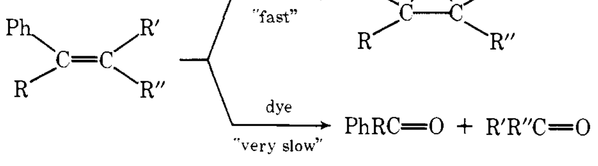
Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. *Received November 13, 1975*

Abstract: Photooxidation of nine olefins in benzene solution with oxygen and benzil leads to epoxides as the main product in yields ranging from 5% in 60 min for *trans*-stilbene to 98% in 15 min for norbornene. From cis or trans acyclic olefins the epoxide is always trans. Competing processes include formation of allylic hydroperoxides from olefins (2,3-dimethyl-2-butene and 1,2-dimethylcyclohexene) that are quite reactive toward singlet oxygen, and energy transfer with cis,trans isomerization of olefins with lower lying triplet states (stilbene). Recovery of benzil is high, showing that it is neither consumed stoichiometrically in the process nor oxidized directly in effective competition with the photoepoxidation. The action of biacetyl as a photosensitizer is similar to that of benzil but is attended by much more destruction of the diketone and yields epoxide with a wider range of olefins. Seven of the 18 olefins in Table III are converted to epoxides in yields of 90% or more, making this a useful preparative method. Benzil and biacetyl are compared with the π,π^* photosensitizer fluorenone, which can produce singlet oxygen but gives no epoxidation, and with the n-π^* sensitizer benzophenone, in which cycloaddition to an olefin to give oxetane is an important competing process and becomes the major course of the reaction with norbornene. The nature of the mechanism is discussed.

Dye-sensitized photooxidation reactions have been extensively investigated and the results are consistent with the singlet oxygen mechanism.[1] Photooxidation with n-π^* triplet sensitizers, however, presents a less simple picture. A free-radical mechanism is indicated in benzophenone-sensitized oxidation of 2-propanol.[2] Gollnick and co-workers have pointed out that n-π^* triplet sensitizers can also generate singlet oxygen.[3] We report here the results of photooxidation of various olefins with benzil and biacetyl as sensitizers and show that the present photooxidation is quite different from the singlet oxygen oxidation and also from radical-chain autoxidations.

Photooxidation with Benzil. The irradiation[4] of a benzene solution of 1,2-dimethylcyclohexene (**1,** 0.5 M) and benzil (0.1 M) with a Hanovia 450-W medium-pressure mercury lamp at 0° for 15 min, oxygen being bubbled through during the irradiation, gave allylic hydroperoxide (**2a**) and epoxide (**3**) in 58 and 12% yield, respectively, together with 30% of recovered olefin. Benzil was recovered almost quantitatively. Table I shows the contrast between these results and either the dye-sensitized oxidation[5-7] or the autoxidation reaction.[7,8]

Important differences between dye and benzil sensitizations appear also in the oxidation of aromatic olefins. Benzil-sensitized oxidation of five aromatic olefins gave epoxides as shown in Table II, whereas it is known that these aromatic olefins are converted very slowly to ketones by long exposure to singlet oxygen.[9] A characteristic feature is the stereochemistry of epoxide formation: only *trans*-epoxide was obtained independently of the geometry of the starting olefins. Photoepoxidation also occurred in norbornene or 3,3-dimethyl-1-butene, which has no active allylic hydrogen. In the case of the reaction of 2,3-dimethyl-2-butene, an equimolar amount of Dabco quenched both formation of allylic hydroperoxide and epoxide completely. 2-Methyl-2-butene gave only allylic hydroperoxides with benzil photosensitization.

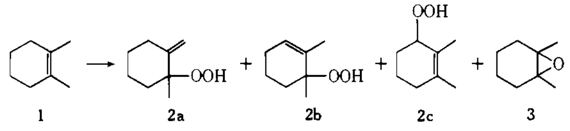


Photooxidation with Biacetyl. Biacetyl is known to be photooxidized, with cleavage between the carbonyl groups, at a rate that depends upon the medium.[10] In the presence of olefins, a rapid epoxidation competes with the photodecomposition of biacetyl, amounting to an efficient general preparative method for the corresponding epoxides. For 14 alkenes in Table III, 1 mol of biacetyl will bring about the epoxidation of from 1 to 2 mol of alkene; thus, the oxidative destruction of the diketone is a strongly competing process but is not stoichiometrically involved in the epoxidation. Dr. M. J. Shapiro has found that the related diketone 1-phenyl-1,2-propanedione, which resembles biacetyl in reactivity, converts 3 mol of 1,1-diphenyl-2-methylpropene to its epoxide.[11]

A typical experimental procedure is the preparation of 1,2-epoxy-2-methyl-1,1-diphenylpropane (**5**). A benzene solution (15 ml) containing 5 mmol each of biacetyl and 2-methyl-1,1-diphenylpropene (**4**) was continuously saturated with oxygen in a Pyrex glass cell and irradiated with a Hanovia 450-W medium-pressure mercury lamp at 0° for 30 min. The biacetyl was completely consumed. The almost colorless reaction mixture was washed with sodium bicarbonate solution and the benzene layer was concentrated at reduced pressure. The residual oil was chromatographed over alumina (30 g) and the product eluted with *n*-pentane. Removal of the solvent yielded almost pure epoxide **5** as a colorless solid, mp 61-62 °C (lit.[3] 61-62 °C), in 98% yield. For preparation of volatile epoxides, *o*-dichlorobenzene was used as solvent. The crude reaction mixture was washed with sodium bicarbonate solution and the organic layer was passed through a short column of alumina, followed by elution with more *o*-dichlorobenzene. The volatile epoxides were collected by fractionation under reduced pressure. In this procedure the bicarbonate wash removes acetic acid, a major product from the biacetyl, while many minor products are removed by retention on the alumina. The results of epoxidation of various olefins are given in Table III. In the absence of olefin, biacetyl decomposed completely within 1 h under the above conditions, whereas less than 5% of the decomposition took place during equal irradiation time, under an atmosphere of argon.

The relative reactivities of the alkenes were measured by product analyses of competing pairs, and the results are included in Table III. The order of reactivity is close to that in benzil photooxidation (Table I), except where the products are quite different. 2,3-Dimethyl-2-butene, which yields 93% al-

Table I. Types of Oxidation of 1,2-Dimethylcyclohexene (**1**) by Oxygen



	2a	**2b**	**2c**	**3**
Polymer-Rose bengal[a]	87	13	0	0
Soluble sensitizer[b]	89	11	0	0
Soluble sensitizer[c]	90	10	0	0
Soluble sensitizer[d]	97	3	0	0
$(PhO)_3PO_3$[d]	96	4	0	0
Radical autoxidation[b]	6	39	54	0
Benzil	83	0	0	17

[a] A. P. Schaap, A. L. Thayer, E. C. Blossey, and D. C. Neckers, *J. Am. Chem. Soc.*, 97, 3741 (1975). [b] C. S. Foote, *Acc. Chem. Res.*, 1, 104 (1968). [c] W. Fenical, D. R. Kearns, and P. Radlic, *J. Am. Chem. Soc.*, 91, 7772 (1969). [d] R. W. Murray, J. W.-P. Lin, and M. L. Kaplan, *Ann. N.Y. Acad. Sci.*, 171, 121 (1970).

Table II. Benzil-Sensitized Photooxidation of Olefins[a]

Olefin	Time, min	Rel[b] reactivity	Products, %
cis-$PhCH{=}CHCH_3$ (c-6)	15		*trans*-Epoxide (7), 89
trans-$PhCh{=}CHCH_3$ (t-6)	15	1.0	*trans*-Epoxide (7), 96
$Ph_2C{=}C(CH_3)_2$ (4)	15	0.5	Epoxide (5), 80
cis-$PhCh{=}CHPh$ (c-10)	60		*trans*-Epoxide (11), 5 Recovered stilbene, 59[c]
Norbornene (8)	15	0.6	*exo*-Epoxide (9) 98
trans-$PhCH{=}CHPh$ (t-10)	60	<0.01	*trans*-Epoxide (11), 5 Recovered stilbene, 66[d]
$H_2C{=}CHC(CH_3)_3$ (14)	120	<0.01	Epoxide (15), 69 Recovered olefin, 22
$(CH_3)_2C{=}C(CH_3)_2$ (16)	15	>100	$H_2C{=}C(CH_3)_2$ OOH (17), 93 Epoxide (18), 7
$(CH_3)_2C{=}CHCH_3$	30		$CH_2{=}CHC(CH_3)_2$-OOH, 65 $CH_2 = C(CH_3)CH$-$(OOH)CH_3$, 35
$(CH_3)_2C{=}C(CH_3)_2$ + Dabco	15		None
$Ph_2C{=}CH_2$ (**12**)	60		Epoxide (**13**), 31 Benzophenone, 31
trans-$PhCH{=}CH$-$COCH_3$	60		Recovered olefin, 100 cis/trans = 1.7

[a] A benzene solution of equimolar amounts of olefin and benzil (0.10 M) was irradiated at 0°. [b] By competition experiments. [c] Cis/trans = 12. [d] Cis/trans = 6.

Table III. Photoepoxidation with Biacetyl and Oxygen[a,h]

Olefin	Rel reactivity	Time, h	% yield[b] of epoxide
2,3-Dimethyl-2-butene	1.4	0.5	75[c,e]
Norbornene	1.0	0.5	98
cis-2-Pentene[f]		1	71 (t/c = 6)[c,e]
3,3-Dimethyl-1-butene	0.02	1.5	72[c,e]
4-Methyl-1-hexene		1.5	90
Isopropenyl acetate		1	95
1,7-Octadiene		1	63 + diepoxide (15)
Cyclohexene		1.5	79[d]
trans-β-Methylstyrene	(1.0)	0.5	95 (trans)
cis-β-Methylstyrene		0.5	89 (trans)
α-Methylstyrene	0.83	0.5	54 + acetophenone (36)
p-Methylstyrene	0.75	0.5	91
1,1-Diphenylethylene	0.54	0.5	53 + benzophenone (24)
2-Methyl-1,1-diphenylpropene	1.2	0.5	98
trans-Stilbene[g]	0.07	1	90 (trans)
cis-Stilbene		1	65 (trans)
cis-Stilbene[g]		1	89 (trans)
Ethyl cinnamate[g]	<0.02	1	78 (trans)
Benzalacetone[f]		3	60 (trans)

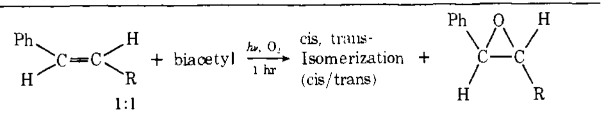
[a] In benzene, unless otherwise noted (biacetyl:alkene 1:1 unless noted). [b] Isolated yield. [c] In *o*-dichlorobenzene. [d] In dichloromethane. [e] The NMR analysis of the crude reaction mixture showed that the oxirane formation was almost quantitative. [f] Biacetyl/alkene = 2. [g] Biacetyl/alkene = 5. [h] All epoxides were identified by comparison with specimens prepared by epoxidation with *m*-chloroperbenzoic acid.

lylic hydroperoxide with benzil, shows a reactivity more than 100 times that of *trans*-β-methylstyrene in Table I; but toward photooxidation by biacetyl, where the product is only epoxide, its relative reactivity (Table III) is 1.4, still less than the partial reactivity factor of seven estimated from Table I for epoxide only. Although we might suspect from this result that biacetyl is incapable of yielding singlet oxygen, the cases of 1,1-diphenylethylene and α-methylstyrene, yielding 24 and 36%, respectively, of ketonic cleavage product, would be compatible with the view that in most of the olefins of Table III an extremely rapid reaction of excited ketone with olefin bypasses the energy transfer to oxygen and initiates the sequence of reactions leading to the epoxide.

As in benzil photooxidation, both cis and trans alkenes yield epoxides of predominantly trans configuration. This is not the result of a prior photoisomerization of the alkene, since in several clear cases the photoisomerization is from trans to cis, whereas the final epoxide is trans.

The last four alkenes in Table III are exceptional in requiring more than 1 mol of biacetyl to photooxidize 1 mol of alkene. In the case of stilbene, the triplet excitation energy of biacetyl (55 kcal) lies between those of the cis and trans isomers of the olefin (57 and 50, respectively).[12] These relations result in a curious pattern of reactivity: if *trans*-stilbene is irradiated under oxygen for 1 h with equimolar biacetyl, the yield of epoxide is only 6%, but a mixture of *cis*- and *trans*-stilbene is recovered (86%) in the isomer ratio of 6.2:1 by the time the biacetyl is exhausted. In the presence of a fivefold excess of biacetyl, irradiation for the same length of time yields *trans*-stilbene oxide in 90% yield. That *cis*-stilbene is more efficiently converted to *trans*-epoxide under these conditions than is *trans*-stilbene is shown by its yielding 65% of *trans*-stilbene oxide when irradiated for 1 h in the presence of only 1:1 biacetyl. Evidently the pattern of triplet energies causes initial energy transfer to *trans*-stilbene. Following the photochemical trans,cis isomerization, the resulting *cis*-stilbene is available for epoxidation, since its triplet excitation energy is too high to make it a rapid energy acceptor from the oxidizing species or quencher of the sensitizer. These results tell us that, whereas the isomerization may proceed through the excited triplet alone, the epoxidation step itself involves an intermediate *biradical* in which rotation from cis to trans conformation is overwhelmingly probable. The similar behavior of ethyl cinnamate and benzalacetone is shown in Table IV.

Table IV. Initial Behavior of Low Triplet Energy Alkenes in Biacetyl Photooxidation



R = Ph	86% (6.2)	6%
R = $CO_2CH_2CH_3$	97% (2.0)	2%
R = $COCH_3$	93% (1.6)	~1%

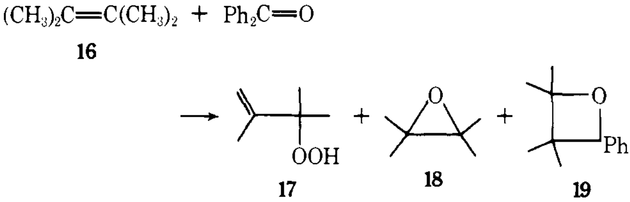
Table V. Photooxidation of 2,3-Dimethyl-2-butene

		Relative yield, %	
Sensitizer	Solvent	Hydro- peroxide	Epoxide
Tetraphenylporphin	CH_2Cl_2	100	0
Benzil	Benzene	93	7
Biacetyl	Benzene	0	100
1-Phenyl-1,2-propanedione	Benzene	0	100

Although singlet oxygen appears to be capable of yielding some epoxide as well as dioxetane from hindered alkenes,[13] bona fide singlet oxygen, from chemical sources or from dye-sensitized photooxidation, yields only allylic hydroperoxide from tetramethylethylene, showing that the present epoxidation does not involve singlet oxygen. Table V shows that, despite many similarities in behavior between biacetyl and benzil, they behave quite differently in photooxidation of tetramethylethylene, the benzil product being consistent with the involvement of competing singlet oxygen.

\ **Photooxidation with Fluorenone.** Fluorenone as a photosensitizer behaved like the sensitizing dyes in that it converted tetramethylethylene cleanly to its allylic hydroperoxide, but showed hardly any reactivity toward the aromatic olefins.

Photooxidation with Benzophenone. Benzophenone differs from fluorenone most notably in its excitation, as with the α-diketones, to an n–π* triplet. Irradiation of a benzene solution of benzophenone and fourfold excess of 2,3-dimethyl-2-butene, saturated with oxygen, for 3.5 h gave a mixture of hydroperoxide (**17**), epoxide (**18**), and oxetane (**19**) in 96, 11, and 75% relative yields, respectively. Comparable experiments showed that the oxetane formed more rapidly under oxygen than under an argon atmosphere when other conditions were identical (Table VI). The ratio of hydroperoxide (**17**) to oxetane (**19**) decreased with increasing concentration of olefin, whereas the ratio of the oxetane formation under oxygen to that under argon increased at the higher concentration of olefin. Dabco partially quenched the formation of oxetane as well as oxidation products, but did not change the ratio of allylic hydroperoxide to oxetane. This indicates that the quenching involves the excited ketone, as in the benzil reactions, and not selectively singlet oxygen, for which Dabco is also a quencher.[14] Benzophenone-sensitized oxidation of biadamantylidene gave epoxide and 2-adamantanone in 44 and 39% yield, respectively, whereas aromatic olefins such as β-methylstyrene were inactive except for cis,trans isomerization, evidently as a result of effective energy transfer from excited benzophenone to olefin.



$(CH_3)_2C{=}C(CH_3)_2 + Ph_2C{=}O$

16

17 **18** **19**

Discussion

In the photosensitization with benzil the results can be examined first with reference to the general reactivity of the olefinic substrate toward singlet oxygen. The most reactive, tetramethylethylene, yields the same allylic hydroperoxide as in dye-sensitized photooxidation or in reaction with thermally generated singlet oxygen. The product of the less reactive 1,2-dimethylcyclohexene includes 83% of the hydroperoxide **2a,** which is the main product in singlet oxygen oxidation,[15] along with 17% of epoxide, while the aryl olefins, which do not

Table VI. Photooxidation with Benzophenone as Sensitizer[a]

Mol/l.			React.	Mol/l,			19 (O_2)/	
Olefin	Ph_2CO	Dabco	condn	17,[b] M	18, M	19,[c] M	19 (Ar)	17/19
				2,3-Dimethyl-2-butene (**16**)				
0.100	0.100		Ar			0.012		
0.100	0.100		O_2	0.030	0.002	0.016	1.3	1.9
0.100	0.100	0.100	O_2	0.0088		0.0049		1.8
0.500	0.100		Ar			0.015		
0.500	0.100		O_2	0.0315		0.0345	2.3	0.9
				Biadamantylidene (20)[d]				
0.200	0.200		O_2	Products: epoxide (**21**) (44%) adamantanone (**22**) (39%)				
				Norbornene (8)				
0.80	0.20		O_2	*exo*-Epoxide (9) (13%), *exo*-oxetane (**23**) (20%)				
0.80	0.20		Ar	*exo*-Oxetane (**23**) (29%)				
				cis-2-Butene (c-24)				
See Experimental Section			O_2	Allylic hydroperoxide (75%), isomeric oxetanes (34) 4.0:1 (30%)				
			Ar	Isomeric oxetanes (34) 3.3:1 (24%)				
				trans-2-Butene (t-24)				
See Experimental Section			O_2	Allylic hydroperoxide (125%), isomeric oxetanes (34) 4.3:1 (37%)				
			Ar	Isomeric oxetanes (34) 3.0:1 (20%)				
				2-Methyl-2-butene				
0.200	0.100		O_2	Isomeric hydroperoxides 1.8:1 (24%) Isomeric oxetanes 8:1 (44%)				
			Ar	Isomeric oxetane 8:1 (35%)				

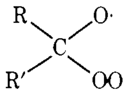
[a] Irradiation was carried out in benzene solution in a merry-go-round at 0° for 15 min. [b] Determined by NMR analysis. [c] Isolated yield. [d] In carbon tetrachloride.

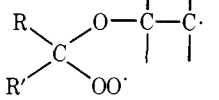
react in this length of time with free singlet oxygen, yield epoxide as the sole product. Since benzil and benzophenone triplets (E_T = 54 and 69 kcal/mol) have ample energy[3] to generate free singlet oxygen, the simplest account of the present results is to say that there is concurrent generation of free singlet oxygen and operation of a second, in this case slower, mechanism leading to epoxide in those olefins in which reactivity toward singlet oxygen is low.

The formation of only the *trans*-epoxide from either *cis*- or *trans*-alkene requires a stepwise mechanism by way of a freely rotating intermediate,[16] in contrast to epoxidation with peracids. For this process a mechanism is required that converts the double bond to a single bond in the intermediate and delivers only a single oxygen atom to the acceptor site.

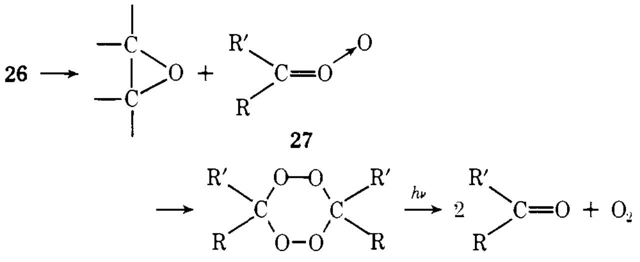
An attractive hypothesis for the photooxidation that yields epoxides from $^1O_2$[18,19] in the cases of the very hindered alkenes is the competitive reaction of an initially formed perepoxide[20] with a second singlet oxygen molecule to yield epoxide and ozone, the latter being recycled since its reaction with binorbornylidene and biadamantylidene yields only epoxide again.[13,18] Some of the more obvious kinetic properties of binorbornylidene photoepoxidation are in favor of this sequence,[18,19] and it is supported by MO calculations.[21] Our present results, however, include photoepoxidations of a number of unhindered alkenes that react normally and rapidly with ozone; the perepoxide–ozone hypothesis would require that the products from most of our alkenes should include ozonides, ketones, and aldehydes in amounts comparable to the epoxides found, and this is far from being the case.

If either a π exciplex of ketone and oxygen or a σ biradical (**25**) were to attach to an alkene, the "best" biradical might


25

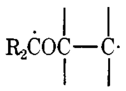

26

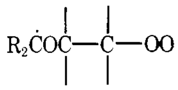
be formed by reaction at the single oxygen atom as in **26** rather than at the peroxy group. Cleavage of this species to epoxide and carbonyl oxide (**27**) would be a possible sequence; in an aprotic solvent the carbonyl oxide of a simple ketone could dimerize to cyclic peroxide (**28**), which might fragment photochemically to ketone and molecular oxygen.[22,23]


27

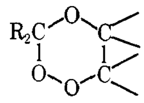
28

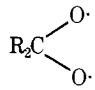
Another reasonable sequence for the formation of a biradical intermediate is the initial bond formation between ketone and alkene to give **29**, followed by the attachment of oxygen to the other alkene carbon, producing **30**, an isomer of **26**. The re-


29


30

activity of **29** toward oxygen at its carbon radical end is beyond doubt, but in order to fragment into epoxide and any other plausible product **30** would have to rearrange through cyclization to **31**, and even in the fragmentation of **31** to epoxide and carbonyl, oxide **26** would lie on the most likely reaction path.


31

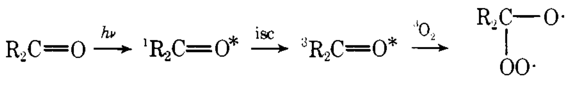

32

One conceivable advantage of a sequence involving **31** is that by initial cleavage at the peroxide bond, it could fragment into epoxide and the methylene dioxide structure **32** which, according to the calculations of Wadt and Goddard,[24] should be of lower energy than the carbonyl oxide **27**.

Benzil is itself subject to photooxidation in benzene, yielding phenyl benzoate, biphenyl, and benzoic acid as the principal products.[25] However, the recoveries of benzil in Table II show that the photooxidation of benzil in the presence of reacting olefin is much slower than the oxidation of the olefin, and some cycle for the regeneration of benzil must be operating. With biacetyl as initiator the decomposition of the diketone is faster, but still not stoichiometric.

Fluorenone and benzophenone both behave as if capable of generating singlet oxygen when in the presence of the reactive substrate, tetramethylethylene. Benzophenone, however, also adds to the double bond to give oxetanes, a behavior not shown by either fluorenone or benzil. Toward the β-methylstyrene isomers benzophenone transfers excitation energy, resulting in the cis,trans isomerization of the olefins, but no other reaction. The inability of fluorenone to do this is evidently a consequence of its low triplet energy (E_T = 53 kcal/mol) compared to benzophenone; however, the failure of fluorenone to yield oxetanes by addition to olefins may be a result of the π–π* nature of the fluorenone triplet which, lacking free radical character on the oxygen, enters into neither photoreduction nor oxetane formation.[26] These comparisons lend credence to the notion that the efficient epoxidation mechanism seen in benzil, benzophenone, and biacetyl grows out of the n–π* character of the lowest triplet states of these ketones and is a biradical sequence.

Although much more experimentation is needed to define these photooxidation mechanisms completely, it is interesting to speculate on the meaning of the product distributions in the benzophenone-sensitized reaction (Table VI). The yield of oxetane under argon is essentially independent of olefin concentration over a fivefold range. So is the yield of allylic hydroperoxide under oxygen. However, in the oxygen-saturated system a fivefold increase in olefin concentration brings about almost a doubling in the yield of oxetane, and not at the expense of the allylic hydroperoxide. A process that could give oxetane, but no singlet oxygen, might be formation of a ketone–oxygen exciplex independently of the direct formation of excited ketone. The reactions would lead to **25** in both cases. However, the **25** formed via the exciplex would be in the triplet


$$R_2C{=}O \xrightarrow{h\nu} {}^1R_2C{=}O^* \xrightarrow{\text{isc}} {}^3R_2C{=}O^* \xrightarrow{^1O_2} \begin{matrix} R_2C{-}O\cdot \\ | \\ OO\cdot \end{matrix}$$

25 (singlet)

$$R_2C{=}O + {}^3O_2 \xrightarrow{h\nu} 3[R_2C{=}O\cdot O_2]^* \longrightarrow \mathbf{25}\ \text{(triplet)}$$

state and would easily attack olefin to form triplet **26**, leading most easily to oxetane and ground-state oxygen, whereas the **25** from triplet benzophenone and ground-state oxygen would be in the singlet state and would be merely a possible intermediate in the formation of singlet oxygen and ground-state ketone. Since triplet **25** could also cleave in a quenching process, the amount of it captured by olefin would be proportional to the olefin concentration and would not be at the expense of the singlet oxygen.

Several pertinent questions arise concerning the α-diketone photoepoxidation: (1) Why are α-diketones especially effective? (2) Why are both epoxidation and ketone destruction so much faster with biacetyl than with benzil? (3) What is the significance of the order of reactivity of alkenes in photoepoxidation? A suggestive feature of the structure of an α-diketone is that the π and π^* orbitals, in the coplanar conformation, extend over both carbonyl groups and offer delocalization both in the excited diketone (evident in the low E_T value) and in the carbonyl oxide, which should lower the energy for elimination of epoxide from **26.** Hindrance to the conformational requirements of this process should be less severe with biacetyl than with benzil, and the initial cross-excitation with molecular oxygen would presumably be faster in the former case.

As to the reactivity order of alkenes, it is obvious that it is not the order of activity toward singlet oxygen, but this reactivity order does not clearly establish the free radical nature of attack on the double bond. *p*-Methylstyrene, which polymerizes actively under free radical initiation, is somewhat less reactive than 2-methyl-1,1-diphenylpropene, a tetrasubstituted olefin not subject to free-radical polymerization at all. However, free-radical initiation of polymerization is a poor general criterion for the ability of free radicals to attack the double bond, since the hindered step in polymerization must often be the bond formation between two monomer molecules, which is no part of the present epoxidation sequence.

Experimental Section

Infrared spectra were run on a Beckman IR-30 spectrometer. NMR spectra were obtained on a Varian A-60 spectrometer using Me_4Si as an internal standard. Analytical VPC was carried out on an F & M 700 gas chromatograph, and a Varian Aerograph Model 90-P was used for preparative purposes.

Benzil, benzophenone, benzalacetone, biacetyl, *cis*-2-butene, cyclohexene, 1,4-diazabicyclo[2.2.2]octane (Dabco), 2,3-dimethyl-2-butene, 1,2-dimethylcyclohexene, 3,3-dimethyl-1-butene, 1,1-diphenylethylene, 1,1-diphenyl-2-methylpropene, *p*-methylstyrene, *cis*- and *trans*-1-phenylpropene, 1-phenylpropane-1,2-dione, norbornene, isopropenyl acetate, *cis*- and *trans*-stilbene, *cis*- and *trans*-2-butene, fluorenone, tetraphenylethylene, 2-methyl-2-butene, and tetraphenylporphin were obtained from commercial sources.

General Photooxidation Procedure. A benzene solution (0.1–0.5 M) of olefin and ketone in a Pyrex glass test tube (18 × 150 mm) was saturated by bubbling oxygen for 15 min at 0°. The solution was then irradiated with a Hanovia 450-W, medium-pressure mercury lamp at 0°, oxygen being bubbled through during the irradiation. The products were isolated by column chromatography over alumina and/or preparative VPC using columns packed with 20% SE-30 on Chromosorb P (SE-30) or 20% Carbowax 20M on Chromosorb W (CW) and were identified by comparison with the authentic samples prepared separately. This procedure was used in all photooxidations unless otherwise indicated.

Photooxidation of 1,2-Dimethylcyclohexene (1) with Benzil. A benzene solution (2 ml) containing 1 mmol of **1** and 0.2 mmol of benzil was irradiated for 15 min. The NMR spectrum of the crude mixture showed two sharp singlets at δ 1.2 and 1.3 in a ratio of 1:2.4. The solution was distilled at reduced pressure (0.1 mm). Benzil was recovered in 94% yield by recrystallization of the residual yellow solid from pentane. The distillate was passed through a short column of alumina (10 g) at 0°. The eluent contained only one product besides the unchanged olefin on GLC (1.5 ft, CW at 90°; retention times of the olefin and the product were 2.4 and 6.6 min, respectively), and it was isolated by preparative GLC. This was identified as 1,2-epoxy-1,2-dimethylcyclohexane (**3**) by comparison with an authentic sample prepared from **1** and *m*-chloroperbenzoic acid, bp 150–152 °C (lit.[27] 150–150.5 °C): NMR (CCl_4), δ 1.20 (s, 6 H), 1.32–1.85 (m, 8 H). Elution with 10% ether in methylene chloride gave a colorless oil which was shown to be 2-methylmethylenecyclohexane 2-hydroperoxide (**2a**) by comparison with an authentic sample prepared by tetraphenylporphine-sensitized oxidation of **1**;[1b] NMR (CCl_4), δ 1.35 (s, 3 H), 1.5–2.4 (m, 8 H), 4.83 (br s, 2 H). The yields of **2a** and **3** were determined by NMR analysis to be 57 and 12%, together with 30% of the initial olefin (**1**). Longer irradiation caused significant decomposition of both **2a** and **3** to give many unidentified materials.

Photooxidation of 1,1-Diphenyl-2-methylpropene (4) with Benzil. A benzene solution of an equimolar amount (2 mmol) of the olefin and benzil was irradiated for 15 min. Solvent was removed by a rotary evaporator and the residue was chromatographed over alumina (50 g). Elution with pentane gave a colorless solid, mp 61–62 °C (80%), which was shown to be 1,2-epoxy-1,1-diphenyl-2-methylpropane (**5**) by comparison with an authentic sample prepared from perbenzoic acid and **4**, mp 61–62 °C (lit.[28] 61–62 °C); NMR (CCl_4), δ 1.11 (s, 6 H), 7.04–7.49 (m, 10 H). Elution with benzene gave benzil in 75% recovery.

Photooxidation of *cis*- and *trans*-1-Phenylpropene with Benzil. A benzene solution of an equimolar amount (2 mmol) of *cis*-**6** and benzil was irradiated for 15 min. Solvent was removed and the residue was chromatographed over alumina (50 g). Eluting with pentane gave a colorless oil which was identified as *trans*-1,2-epoxy-1-phenylpropane (89%) by comparison with authentic samples of *cis*- and *trans*-**7** prepared by epoxidation with *m*-chloroperbenzoic acid; *trans*-**7**, bp 85–86 °C (13 mm) (lit.[29] 88 °C (13 mm)); NMR (CCl_4), δ 1.37 (d, J = 5 Hz, 3 H), 2.80 (quartet (J = 5 Hz) of d (J = 2 Hz), 1 H), 2.38 (d, J = 2, Hz, 1 H), 7.13 (s, 5 H); *cis*-**7**, bp 83–84 °C (13 mm) (lit.[29] 83–84 °C (13 mm)), NMR (CCl_4), δ 1.00 (d, J = 5 Hz, 3H), 3.12 (quartet (J = 5 Hz) of d (J = 4 Hz), 1 H), 3.87 (d, J = 4 Hz, 1 H), 7.17 (s, 5 H). Elution with 5% ether in benzene gave benzil (93% recovery).

Irradiation of an equimolar amount (2 mmol) of *trans*-**6** and benzil for 15 min gave *trans*-**7** in 96% yield. Benzil was recovered in 87% yield.

Photooxidation of Norbornene with Benzil. A benzene solution of an equimolar amount (2 mmol) of norbornene and benzil was irradiated for 15 min. Solvent was removed and the residue was chromatographed over alumina (50 g). Elution with pentane gave a colorless oil, which was recrystallized from pentane, mp 120–122 °C (98%), identified as *exo*-2,3-epoxynorbornane (lit.[30] 118–119 °C): NMR (CCl_4), δ 0.65 (br d, J = 10 Hz, 1 H), 1.10–1.55 (m, 5 H), 2.40 (br s, 2 H), 2.87 (s, 2 H). Benzil was recovered in 94% yield by eluting with methylene chloride.

Photooxidation of *cis*- and *trans*-Stilbene with Benzil. Equimolar amounts (2 mmol) of *cis*-stilbene and benzil in benzene were irradiated for 1 h. Solvent was removed and the residue was chromatographed over alumina (50 g). Elution with pentane gave a colorless oil. Elution with benzene yielded benzil in 69% recovery. Rechromatographing the first oil over alumina (100 g) and eluting with pentane gave isomeric stilbene (cis/trans = 12) and *trans*-stilbene oxide, mp 66–67 °C (lit.[31] 68 °C): NMR (CCl_4), 3.67 (s, 2 H) and 7.22 (s, 10 H) in 59 and 7% yield, respectively. Similarly, *trans*-stilbene was irradiated under identical conditions mentioned above. Isomeric stilbenes (cis/trans = 6) and *trans*-epoxide (**11**) were isolated in 66 and 5% yield, respectively. Benzil was recovered in 62% yield. In both cases, a trace amount of benzaldehyde was detected in the crude reaction mixture.

Photooxidation of 1,1-Diphenylethylene with Benzil. Equimolar amounts (2 mmol) of the olefin and benzil were irradiated for 1 h. Solvent was removed and the residue was chromatographed over alumina (100 g). Eluting with pentane gave a colorless oil, which was recrystallized from pentane, mp 53–56 °C, the NMR spectrum of which was identical with that of 2,2-diphenyloxirane (**13**) prepared by epoxidation with *m*-chloroperbenzoic acid, mp 55–56 °C (lit.[32] 55–55.5 °C): NMR (CCl_4), δ 3.02 (s, 2 H), 7.18 (s, 10 H). The yield was 31%. Elution with benzene gave benzophenone and benzil in order of elution in 31 and 91% yields, respectively.

Photooxidation of 3,3-Dimethyl-1-butene with Benzil. A benzene solution of equimolar amounts (2 mmol) of olefin and benzil was irradiated for 2 h. The solution was distilled under reduced pressure by water aspirator. Recrystallization of the residue from pentane gave benzil in 79% recovery. The distillate contained one product besides the unchanged olefin. The product was collected by preparative GLC (5 ft, CW at 120°) and was identified as *tert*-butyloxirane (**15**) by comparison with an authentic sample prepared from **14** with *m*-chloroperbenzoic acid, bp 35–36 °C (40 mm) (lit.[33] 89–90.5 °C): NMR (CCl_4), 0.90 (s, 9 H), 2.44–2.66 (m, 3 H). The yield of the epoxide was 69%, along with 22% of the unchanged olefin.

Photooxidation of 2,3-Dimethyl-2-butene with Benzil. A benzene solution of an equimolar amount (2 mmol) of 2,3-dimethyl-2-butene and benzil was irradiated for 15 min. The reaction mixture was distilled under reduced pressure (1 mmHg). Recrystallization of the residual solid gave benzil (90%). The distillate was washed with 1 N sodium hydroxide solution. The water layer was acidified with dilute hydrochloric acid, extracted with ether, and dried over magnesium sulfate. Evaporation of the solvent left a colorless oil, which was shown to be 3-hydroperoxy-2,3-dimethyl-1-butene (**17**) by comparison with an authentic sample prepared by photooxidation of **16** using tetraphenylporphine as a sensitizer, bp 56–58 °C (13 mm) (lit.[34] 55 °C (12 mm)): NMR (CCl_4) δ 1.23 (s, 6 H), 1.72 (m, 3 H), 4.81 (m, 1 H), 4.87 (m, 1 H). The benzene layer was analyzed by GLC and NMR. The only detectable product was shown to be 2,3-epoxy-2,3-dimethylbutane (**18**) by comparison with an authentic sample prepared from **16** with *m*-chloroperbenzoic acid, bp 90–91 °C (lit.[35] 90–93 °C): NMR (benzene) δ 1.15 (s, 12 H). The yields of **17** and **18** were 93 and 7%, respectively, by NMR analysis.

A benzene solution (0.100 M) of **16**, benzil, and Dabco was irradiated for 15 min. Significant reaction could not be detected by NMR analysis. No oxidation product could be observed on GLC.

Competition Experiment in Photooxidation with Benzil. A benzene solution of equimolar amounts (1.00 mmol) of *trans*-1-phenylpropene and an olefin was irradiated for 10 min. The product distribution was determined by NMR analysis.

Photooxidation of Benzalacetone and Tetraphenylethylene. A benzene solution of equimolar amounts (1 mmol) of benzalacetone and benzil was irradiated for 1 h. No reaction could be observed on GLC except cis-trans isomerization of the initial olefin, giving an isomeric mixture (cis/trans = 1.7).

Similarly, irradiation of tetraphenylethylene for 1 h caused no reaction.

Photooxidation of Olefins with Fluorenone. A benzene solution of 5 mmol of 2,3-dimethyl-2-butene and 1 mmol of fluorenone was irradiated for 1 h. The solution was washed with 1 N sodium hydroxide solution. From the benzene layer, fluorenone was recovered in 96% yield. The water layer was acidified with dilute hydrochloric acid, extracted with ether, and dried over magnesium sulfate. Evaporation of the solvent left allylic hydroperoxide (**17**) in 92% yield. Epoxide formation could not be detected on GLC and NMR.

A carbon tetrachloride solution of 5 mmol of norbornene and 1 mmol of fluorenone was irradiated for 1 h. The crude mixture was directly analyzed by GLC; epoxide was formed in 17% yield.

Similarly, equimolar amounts (2 mmol) of 1,1-diphenylethylene and fluorenone were irradiated in benzene for 15 min. No reaction could be detected by GLC.

Photooxidation of Olefins with Tetraphenylporphin. Olefins were irradiated in carbon tetrachloride solution in the presence of a small amount of tetraphenylporphine with a 600-W Quartzline lamp (General Electric) at 0°, oxygen being bubbled through during the irradiation.

Irradiation of 1,2-dimethylcyclohexene and 2,3-dimethyl-2-butene for 15 min gave, respectively, allylic hydroperoxides **2a** and **17** almost quantitatively. Irradiation of *trans*-1-phenylpropene, 1,1-diphenylethylene, *trans*-stilbene, and 3,3-dimethyl-1-butene for 30 min gave no products except a small amount of polymeric material from 1,1-diphenylethylene.

Photooxidation of Olefins with Benzophenone. (a) Photooxidation of 2,3-Dimethyl-2-butene. A benzene solution (10 ml) of 5 mmol of the olefin and 1 mmol of benzophenone was irradiated for 3.5 h. The solution was washed with 1 N sodium hydroxide solution. The water layer was acidified with dilute hydrochloric acid, extracted with 50 ml of ether, and dried over magnesium sulfate. Evaporation of the solvent gave **17**. The benzene layer was distilled under reduced pressure (ca. 1 mm) after drying with magnesium sulfate. The distillate contained one product besides the remaining olefin, which was shown to be the epoxide (**18**) by comparison of the NMR and GLC retention times with those of an authentic sample. The yellow residue was chromatographed over alumina (100 g). Elution with benzene gave a colorless solid which was identified as the oxetane (**19**), mp 122–124 °C (lit.[36] 122–125 °C), 75%; NMR ($CDCl_3$) δ 1.04 (s, 6 H), 1.25 (s, 6 H), 7.04–7.60 (m, 10 H). Elution with 5% ether in pentane gave benzophenone in 19% yield. The yields of **17** and **18** were 19.2 and 2.2%, respectively, by NMR analysis of the crude reaction mixture. The product ratio was checked by NMR at appropriate intervals. The ratio of the oxidation products, **17** and **18**, to the oxetane increased with increasing time of irradiation (time, ratio): 30 min, 1.06; 77 min, 1.24; 183 min, 1.42.

(b) Comparison of Photochemistry of 2,3-Dimethyl-2-butene under Oxygen and under Argon. Two benzene solutions of the olefin (0.10–0.50 M) and benzophenone (0.10 M) were irradiated in a merry-go-round apparatus for 15 min, one being under argon and the other with oxygen bubbling through during the irradiation. Oxidation products were analyzed by NMR and the oxetane was isolated by a procedure similar to that described above.

(c) Quantum Yield of Oxetane Formation under Oxygen. Three benzene solutions were prepared. Each solution was 0.18 M in benzophenone; (a) and (b) were 0.36 M in 2,3-dimethyl-2-butene and (c) was 0.36 M in 2-methyl-2-butene. These three samples were irradiated in a merry-go-round for 1 h at 0° under an argon atmosphere for (a) and (c) but under oxygen for (b). The reaction mixture was directly analyzed by NMR (for oxidation products) and GLC (2 ft SE at 220°).[37] Sample (a) gave 2,2,3,3-tetramethyl-4,4-diphenyloxetane in 12.6% yield. Sample (b) gave the oxetane (**19**), **17**, and **18** in 23.5, 28.1, and 2.2% yield, respectively. The reaction of (c) gave a mixture of oxetane isomers (2,2,3-trimethyl-4,4-diphenyl-oxetane/2,3,3-trimethyl-4,4-diphenyloxetane = 1.0:7.6) in 38.9% yield. Using $\Phi = 0.45$ for the oxetane formation of 2-methyl-2-butene[38] the quantum yield for oxetane formation by 2,3-dimethyl-2-butene was estimated to be $\Phi = 0.15$ under argon atmosphere and $\Phi = 0.27$ under oxygen atmosphere together with $\Phi = 0.32$ for **17** and $\Phi \sim 0.03$ for **18**.

Photooxidation of Biadamantylidene. Equimolar amounts (1 mmol) of biadamantylidene and benzophenone in carbon tetrachloride were irradiated for 1 h. The solvent was removed by evaporation and the residue was chromatographed over alumina (100 g). Elution with pentane gave the unchanged olefin (2%). Elution with 1:1 benzene–pentane gave a colorless solid, mp 182–183 °C, followed by benzophenone, and another colorless solid, mp 250–255 °C, in order of elution. The first solid was shown to be the epoxide (**21**) of biadamantylidene (lit.[39] mp 183–184 °C) and the latter solid to be 2-adamantanone (**22**) by comparison with NMR spectra of authentic samples. The yields of the epoxide and 2-adamantanone were 44 and 39%, respectively. Benzophenone was recovered almost quantitatively.

Photooxidation of Norbornene. Equimolar amounts (1 mmol) of norbornene and benzophenone in carbon tetrachloride (15 ml) were irradiated for 1.5 h. The solution was evaporated in a rotary evaporator. The residue was chromatographed over alumina (100 g). Elution with pentane gave *exo*-2,3-epoxynorbornane (**9**) in 7% yield. Elution with benzene gave a colorless solid, mp 127–128 °C, which was shown to be the oxetane (**23**) (lit.[36] 128–129 °C): NMR (CCl_4), δ 0.79–1.45 (m, 5 H), 1.88 (br d, J = 10 Hz, 1 H), 2.31 (br s, 2 H), 2.78 (d, J = 5 Hz, 1 H), 4.62 (d, J = 4 Hz, 1 H), 7.0–7.5 (m, 10 H).

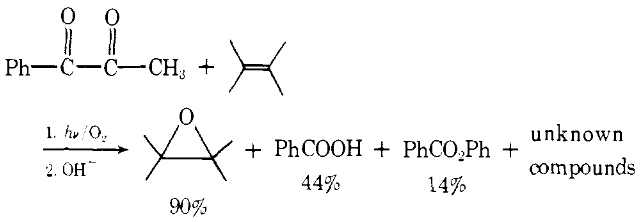
Two benzene solutions of norbornene (0.80 M) and benzophenone (0.20 M) were irradiated in a merry-go-round for 1 h, one being under argon and the other under oxygen. The reaction under argon atmosphere gave **23** in 29% yield, whereas the reaction under oxygen bubbling conditions gave **23** and the epoxide (**9**) in 20 and 13% yields, respectively.

Photooxidation of *cis*- and *trans*-2-Butene. In a Pyrex tube (25 × 250 mm) was placed 20 ml of a 0.2 M benzene solution of benzophenone. The solution was irradiated at 15–20° for 1 h, a mixed gas of oxygen and *cis*-2-butene being bubbled through during the irradiation. The solution was washed with 1 N sodium hydroxide solution. The water layer was acidified with dilute hydrochloric acid, extracted with ether, and dried over magnesium sulfate. Removing the solvent by fractionation left a colorless oil, which was shown to be 3-hydroperoxy-1-butene (**33**): NMR (CCl_4) δ 1.20 (d, J = 6 Hz, 3 H), 4.32 (quintet, J = 6 Hz, 1 H), 5.08 (d of d, J = 11 and 1 Hz, 1 H), 5.12 (d of d, J = 15 and 1 Hz, 1H), 5.5–6.0 (m, 1 H). The benzene layer was evaporated and the residue was chromatographed over alumina (100 g). Elution with 5% benzene in pentane gave a colorless solid, mp 78–86 °C, which was identified as a mixture of stereoisomeric oxetanes (**34**) in a ratio of 4.00:1. Each isomer was isolated by preparative GLC (1.5 ft CW at 160°). The major isomer (A) showed the following NMR: δ 0.83 (d, J = 7 Hz, 3 H), 1.30 (d, J = 6 Hz, 3 H), 3.09 (quintet, J = 7 Hz, 1 H), 4.32 (quintet, J = 6 Hz, 1 H), 7.17 (m, 10 H). The minor isomer (B) showed the following: δ 0.83 (d, J = 7 Hz, 3 H), 1.23 (d, J = 6 Hz, 3 H), 3.50 (quintet, J = 7 Hz, 1 H), 4.89 (quintet, J = 7 Hz, 1 H), 7.15 (m, 10 H). The major isomer has been reported to be the *cis*-oxetane.[26] In a similar procedure, *trans*-2-butene was irradiated for 1 h. Allylic hydroperoxide and the oxetane (A/B = 4.3) were isolated in 125 and 37% yield, respectively (based on the initial mole of benzophenone).

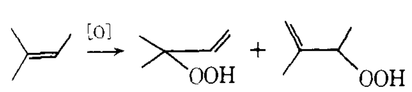
Irradiation under similar conditions, except for bubbling through a mixed gas of *cis*-2-butene and argon instead of oxygen for 1 h, gave the isomeric oxetane (A/B = 3.3) in 24% yield. Similarly, a mixture of isomeric oxetanes (A/B = 3.0) was isolated in 20% yield from the irradiation of *trans*-2-butene under argon.

Photooxidation of 2-Methyl-2-butene. Two benzene solutions of the olefin (0.20 M) and benzophenone (0.10 M) were irradiated in a merry-go-round for 1 h, one (a) being under argon and the other (b) with oxygen bubbling through during the irradiation. A mixture of oxetanes, **36** and **37** in a ratio of 8:1 was isolated in 35% yield from the reaction (a) by chromatographing the crude mixture over alumina and eluting with pentane. The reaction mixture (b) was washed with 1 N sodium hydroxide solution. The organic layer was evaporated and the residue was chromatographed over alumina (100 g). Elution with pentane gave the isomeric oxetanes in 8:1 ratio in 44% yield. The water layer was acidified with dilute hydrochloric acid and extracted with ether. Removing the solvent left a colorless oil, which was shown to be a mixture of allylic hydroperoxides, **38** and **39** (**38**/**39** = 1.8), by comparison of the NMR spectra of the authentic materials obtained by photooxidation of 2-methyl-2-butene with tetraphenylporphine as a sensitizer (**31**/**32** = 1.3). The yield of the peroxide was 24%.

Photooxidation of 2,3-Dimethyl-2-butene with 1-Phenylpropane-1,2-dione. A benzene solution (15 ml) of equimolar amounts (4 mmol) of 2,3-dimethyl-2-butene and 1-phenylpropane-1,2-dione was irradiated with the Hanovia lamp for 30 min, oxygen being bubbled through during the irradiation. The NMR spectrum showed neither dione nor the olefin signals. The epoxide was the sole oxidation product of the olefin and was shown to be formed in 90% yield by NMR analysis. The reaction mixture was washed with potassium carbonate solution. Acidification of the water layer with hydrochloric acid gave benzoid acid (210 mg, 44%). The organic layer was dried over magnesium sulfate and distilled under reduced pressure (13 mm). The residue was chromatographed over alumina (50 g). Elution with benzene gave phenyl benzoate (110 mg, 14%) as a white solid. Elution with 5% methanol in benzene gave 215 mg of unidentified materials. The distillate was analyzed by VPC and the epoxide was identified as the exclusive product from the olefin.



Photooxygenation of 2-Methyl-2-butene. A solution of 500 mg of the olefin and 200 mg of benzil in 10 ml of methylene chloride was irradiated with a Hanovia 450-W mercury lamp at 0° for 30 min, oxygen being bubbled through during the irradiation. The mixture was washed with 20 ml of 1 N sodium hydroxide solution. The water layer was acidified with hydrochloric acid and extracted with ether. Solvent was removed by a rotary evaporator. The residual oil was added carefully to a stirred solution of ether (25 ml) containing a fivefold excess of $LiAlH_4$. The reaction mixture was washed with water and the organic layer was separated. Product distribution was determined by VPC (5 ft 20% Carbowax 20M on Chromosorb P at 100°; retention times of the alcohols were 23.4 and 12.0 min). Relative yields of hydroperoxides **38** and **39**, 65:35.



35 **38** **39**

A solution of 500 mg of the olefin and a small amount of dye sensitizer (ca. 2 mg) in 10 ml of solvent was irradiated with a 600-W tungsten lamp for 30 min at 0°, oxygen being bubbled through during the irradiation. The solvent was removed by a rotary evaporator. The residual oil was added carefully to a stirred solution of ether containing a fivefold excess of $LiAlH_4$. The ether layer was worked up as usual and the products were analyzed by VPC: relative yields of tertiary and secondary hydroperoxides **38** and **39**; with TPP, 56:44; with methylene blue, 58:42.

Photodecomposition of Biacetyl in the Presence of Excess Olefin. (1) A benzene solution (10.0 ml) of 0.57 mmol of biacetyl and 2.40 mmol of 1,1-diphenyl-2-methylpropene was irradiated with a Hanovia 450-W mercury lamp, oxygen being bubbled through during the irradiation. The product distribution was determined by NMR analysis with a JEOL-MH-100 spectrometer (sweep width: 2.7 ppm) at appropriate intervals.

Table VII.

Time, h	Biacetyl, mmol	% Decompn of biacetyl	Olefin, mmol	Epoxide, mmol	Epoxide/biacetyl, mol
(1) 0	0.56	0	2.40	0	
0.12	0.25	57	1.86	0.54	1.7
0.25	0.0	100	1.52	0.98	1.8
0.50	0.0	100	1.51	0.99	1.8
(2) 0	0.50	0	2.45	0	
0.50	0.28	44	2.02	0.43	2.0
0.70	0.26	48	1.96	0.49	2.0

(2) Similarly, a benzene solution (10.0 ml) of 0.50 mmol of biacetyl and 2.45 mmol of the olefin was irradiated with a 600-W tungsten lamp (General Electric Co.), oxygen being bubbled through during the irradiation. Products were analyzed by NMR, and the results are given in Table VII.

Photooxidations with Biacetyl. Photooxidation of *p*-Methylstyrene. A benzene solution (15 ml) of equimolar amounts of the olefin and biacetyl was irradiated for 30 min. The reaction mixture was evaporated by a rotary evaporator. The residue was chromatographed over alumina (50 g). Eluting with pentane gave a colorless oil (91%), which was shown to be the epoxide by comparison with the authentic sample prepared from the olefin and *m*-chloroperbenzoic acid (MCPB), bp 90-93 °C (14 mm) (lit.[40] 51-52 °C (1 mm)): NMR (CCl_4) δ 2.23 (s, 3 H), 2.52 (d of d, $J = 6$ and 4 Hz, 1 H), 2.87 (d of d, $J = 6$ and 2.5 Hz, 1 H), 3.59 (d of d, $J = 4$ and 2.5 Hz, 1 H), 7.0 (s, 4 H).

Photooxidation of 2-Phenylpropene. A benzene solution (15 ml) of equimolar amounts (5 mmol) of the olefin and biacetyl was irradiated for 30 min. Solvent was removed by rotary evaporation. The residue was chromatographed over alumina (100 g), eluting with pentane. There was obtained a colorless oil (54%) and acetophenone (36%), in order of elution. The first product was shown to be the epoxide by comparison with an authentic sample prepared from the olefin and MCBP, bp 80-82 °C (14 mm) (lit.[44] 81-81.5 °C (14 mm)): NMR (CCl_4) δ 1.59 (s, 3 H), 2.57 (d, $J = 5$ Hz, 1 H), 2.78 (d, $J = 5$ Hz, 1 H), 7.18 (s, 5 H).

Photooxidation of Octa-1,7-diene. Equimolar amounts (5 mmol) of the olefin and biacetyl in benzene were irradiated for 1 h. The mixture was washed with saturated sodium bicarbonate solution. The benzene layer was separated and passed through a column of alumina (50 g), eluting with pentane. Solvent was removed by distillation. VPC (4 ft, 20% Carbowax 20M on Chromosorb P, at 160°) analysis of the residue showed three peaks with retention times of 1.2, 13.8, and 31.2 min, the first of which was unchanged diene. The other two compounds were isolated by VPC, and they were shown to be mono- and diepoxide by comparison with the authentic samples prepared by MCPB epoxidation of the olefin. NMR (CCl_4) for monoepoxide: δ 1.42 (m, 6 H), 2.0 (m, 2 H), 2.69 (m, 1 H), 2.28 (d of d, $J = 5$ and 2 Hz, 1 H), 2.54 (d of d, $J = 5$ and 4 Hz, 1 H), 4.86 (d, $J = 10$ Hz, each split to multiplet, 1 H), 4.90 (d, $J = 16$ Hz, each split to multiplet, 1 H), 5.40-6.08 (m, 1 H); ir (liquid film) 1655 cm^{-1}.

For diepoxide, bp 105-108 °C (14 mm) (lit.[41] 120 °C (28 mm)); NMR (CCl_4), δ 1.49 (br s, 8 H), 2.28 (d of d, $J = 5$ and 2 Hz, 2 H), 2.54 (d of d, $J = 5$ and 4 Hz, 2 H), 2.74 (m, 2 H). The yield of the products determined by GLC was 15, 63, and 15% for diene, epoxide, and diepoxide, respectively.

Photooxidation of 2-Acetoxypropene. A benzene solution (15 ml) of equimolar amounts (5 mmol) of the olefin and biacetyl was irradiated for 1 h. The solvent was removed by evaporation and the residue was chromatographed over 100 g of alumina, eluting with pentane. Removing the solvent left a colorless oil, whose spectral data were consistent with the epoxide (95%): NMR (CCl_4), δ 1.64 (s, 3 H), 1.98 (s, 3 H), 2.67 (d, $J = 4.5$ Hz, 1 H), 2.78 (d, $J = 4.5$ Hz, 1 H); ir (liquid film) 1750, 1360, 1230, 1180, 1120, 1100, 1000, 900, 870, and 800 cm^{-1}.

Photooxidation of Ethyl Cinnamate. A benzene solution (15 ml) of 2 mmol of the olefin and 10 mmol of biacetyl was irradiated for 1 h. Solvent was removed by evaporation. The residue was chromatographed over alumina (100 g). Eluting with benzene gave a colorless oil (78%), which was shown to be *trans*-epoxide by comparison of the NMR spectrum with that reported.[42] NMR (CCl_4) δ 1.21 (t, $J = 7$ Hz, 3 H), 3.30 (d, $J = 1.5$ Hz, 1 H), 3.97 (d, $J = 1.5$ Hz, 1 H), 4.13

(quartet, $J = 7$ Hz, 2 H), 7.22 (s, 5 H); ir (liquid film) 1745, 1495, 1460, 1200, 1020, 890, 750, and 690 cm^{-1}.

Equimolar amounts of ethyl cinnamate and biacetyl (5 mmol) in 15 ml of benzene were irradiated for 1 h. NMR analysis showed that the reaction mixture was a mixture of isomeric ethyl cinnamates (cis/trans = 2) (97%) and *trans*-epoxide (~2%).

Photooxidation of 4-Methyl-1-hexene. A benzene solution (15 ml) of equimolar amounts of the olefin and biacetyl was irradiated for 1.5 hr. The solution was washed with saturated sodium bicarbonate solution. The benzene layer was passed through a short column of alumina (20 g), eluting with a small amount of pentane. Removing the solvents left an almost colorless oil, which was shown to be the epoxide by comparison with the authentic sample prepared from 4-methyl-1-hexene and MCPB: NMR (CCl_4) δ 0.8-1.7 (m, 11 H), 2.68 (three doublets, $J = 5.5$, 2.5, and 1.5 Hz, 1 H), 2.42 (t, $J = 5.5$ Hz, each split to d, $J = 1.5$ Hz, 1 H), 2.12 (m, 1 H); ir (liquid film) 1465, 1420, 1385, 1255, 1135, 950, 900, and 830 cm^{-1}.

Photooxidation of *cis*-2-Pentene. An *o*-dichlorobenzene solution (10 ml) of 5 mmol of *cis*-2-pentene and 10 mmol of biacetyl was irradiated for 1 hr. The reaction mixture was washed with sodium bicarbonate solution. The organic layer was passed through a short column of alumina (20 g), eluting with 10 ml of *o*-dichlorobenzene. Fractionation of the eluent gave an oil, bp 78-80 °C (lit.[43] 84 °C) (71%), which was shown to be a mixture of the isomeric epoxides by comparison with the authentic sample of *cis*-epoxide prepared from *cis*-olefin and MCPB: NMR (CCl_4) (peaks due to minor isomer (cis) where resolvable are shown in italics), δ 0.99 (t, $J = 6$ Hz, *3* H), *1.00* (t, $J = 6$ Hz, 3 H), *1.22* (d, $J = 6$ Hz), 1.23 (d, $J = 6$ Hz, 3 H), 1.3-1.65 (m, 2 H), 2.36-2.70 (m, 2 H), *2.70-3.11* (m, 2 H).

Photooxidation of Cyclohexene. A dichloromethane solution (15 ml) of equimolar amounts of cyclohexene and biacetyl (10 mmol) was irradiated with oxygen bubbling for 1.5 h. The solution was evaporated and the residue was chromatographed over alumina (100 g), eluting with pentane. Removing the solvent by fractionation left a colorless oil, which was shown to be the epoxide (79%) by comparison with the authentic sample prepared from the olefin and MCPB, bp 57-58 °C (13 mm) (lit.[45] 54-55 °C (10 mm)): NMR (CCl_4), δ 1.3 (m, 4 H), 1.9 (m, 4 H), 3.12 (s, 2 H).

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the National Institutes of Health for support.

References and Notes

(1) (a) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); (b) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968); (c) W. R. Adams, *Oxidation*, **2**, 65 (1971).

(2) G. O. Schenck, H. D. Becker, K. H. Schulte-Elte, and C. H. Krauch, *Chem. Ber.*, **96**, 509 (1963).

(3) K. Gollnick, T. Franken, G. Schade, and G. Dörhöfer, *Ann. N.Y. Acad. Sci.*, **171**, 89 (1963).

(4) All irradiations were carried out with the same lamp at 0° in a Pyrex glass vessel.

(5) R. W. Murray, J. W-Ping Lin, and M. L. Kaplan, *Ann. N.Y. Acad. Sci.*, **171**, 121 (1970).

(6) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91**, 7772 (1969).

(7) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).

(8) G. O. Schenck, *Angew. Chem.*, **64**, 12 (1952).

(9) The aromatic olefins of Table II were almost inactive toward singlet oxygen during the short periods of exposure reported here (15 min). Cf. G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 3609 (1968).

(10) B. Stevens and J. T. Dubois, *J. Chem. Soc.*, 2813 (1962).

(11) M. J. Shapiro, unpublished work in this laboratory.

(12) G. S. Hammond, J. Saltiel, A. S. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowen, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(13) P. D. Bartlett and M. Ho, *J. Am. Chem. Soc.*, **96**, 627 (1974).

(14) K. Furukawa, E. W. Gray, and E. A. Ogryzlo, *Ann. N.Y. Acad. Sci.*, **171**, 175 (1970); C. Ovannis and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527 (1968).

(15) The significance of the product **2b**, reported in yields from 3 to 13% in singlet-oxygen reactions in various solvents but not detected in the benzil photosensitization, is unclear at present, since its amount is so variable that it may be suspected of being a secondary product. The isomer **2b** may correspond to one of the NMR peaks observed in increasing amounts on prolonged irradiation of **1** with benzil.

(16) In the photoepoxidation of stilbene with benzil, the steady-state olefin mixture is largely cis, while the product epoxide is entirely trans. This eliminates any possibility that the formation of *trans*-epoxide from *cis*-stilbene is due to prior photoisomerization of the excited-triplet olefin.[17]

(17) J. Saltiel, K. W. Neuberger, and M. Wrighton, *J. Am. Chem. Soc.*, **91**, 3258 (1969).

(18) M. Ho, Thesis, Harvard University, Cambridge, Mass., 1974.

(19) P. D. Bartlett, Ingold Lecture, *Chem. Soc. Rev.*, in press.

(20) D. B. Sharp, *Abstracts*, 138th National Meeting of the American Chemical Society, New York, N.Y., Sept 1960, p 79P.

(21) M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, *J. Am. Chem. Soc.*, **97**, 4439 (1975).

(22) P. R. Story, *J. Am. Chem. Soc.*, **90**, 817 (1968).

(23) The possibility may also be considered that the carbonyl oxide might serve as a further epoxidizing agent, but this has been observed only toward the most electron-deficient olefins such as tetracyanoethylene: R. Criegee and P. Gunther, *Chem. Ber.*, **96**, 1564 (1963). The failure of carbonyl oxides to be general epoxidizing agents represents another example of kinetic factors limiting the predictions of thermochemistry, as in the nonobservation of 1,3-dioxolanes from carbonyl oxides[24] and olefins, despite an estimated exothermicity of 100 kcal.

(24) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).

(25) J. Saltiel and H. C. Curtis, *Mol. Photochem.*, **1**, 239 (1969).

(26) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).

(27) D. K. Murphy, R. L. Alumbaugh, and B. Rickborn, *J. Am. Chem. Soc.*, **91**, 2649 (1969).

(28) A. Brodhag and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 3024 (1955).

(29) F. Fischer, *Chem. Ber.*, **89**, 2438 (1956).

(30) H. K. Kwart and W. V. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

(31) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(32) J. Biggs, N. B. Chapman, and V. Wray, *J. Chem. Soc.* **B**, 63 (1971).

(33) C. C. Price and D. D. Carmelite, *J. Am. Chem. Soc.*, **88**, 4039 (1966).

(34) G. O. Schenck and K. Schulte-Elte, *Justus Liebigs Ann. Chem.*, **618**, 185 (1958).

(35) W. J. Hickinbottom and D. R. Hogg, *J. Chem. Soc.*, 4200 (1954).

(36) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

(37) Under these conditions, benzophenone and 2,2,3-trimethyl-, 2,3,3-trimethyl-, and 2,2,3,3-tetramethyl-4,4-diphenyloxetane were well separated with retention times of 15.4, 22.8, 29.4, and 37.2 min, respectively.

(38) P. G. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Am. Chem. Soc.*, **89**, 1967 (1967).

(39) G. B. Gill and D. Hands, *Tetrahedron Lett.*, 181 (1971).

(40) R. Fuchs and C. A. VanderWerf, *J. Am. Chem. Soc.*, **76**, 1631 (1954).

(41) J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

(42) V. R. Velente and J. L. Wolfhagen, *J. Org. Chem.*, **31**, 2509 (1966).

(43) W. J. Hickinbottom, D. Peters, and D. G. M. Wood, *J. Chem. Soc.*, 1360 (1955).

(44) S. Danilow and E. V. Danilowa, *Chem. Ber.*, **60**, 1050 (1927).

(45) G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.*, **26**, 659 (1961).