Table VII

Protic species (HA)	[HA], M	k_{obsd}, sec^{-1}	k_a, M^{-1} sec^{-1}
F_3CCH_2OH	0.39	8.63×10^{-4}	$8.1 \pm 0.2 \times 10^{-4}$
	0.80	12.1×10^{-4}	
	1.20	15.1×10^{-4}	
	1.58	18.1×10^{-4}	
	2.00	21.8×10^{-4}	
	2.40	25.6×10^{-4}	
2-Pyridone	0.254	8.75×10^{-4}	$9.6 \pm 0.4 \times 10^{-4}$
	0.490	11.7×10^{-4}	
	0.770	13.6×10^{-4}	
	1.00	15.4×10^{-4}	
	1.26	17.7×10^{-4}	
	1.48	20.6×10^{-4}	
Phenol	0.270	9.78×10^{-4}	$16.1 \pm 0.6 \times 10^{-4}$
	0.490	13.6×10^{-4}	
	0.753	16.4×10^{-4}	
	0.994	21.6×10^{-4}	
	1.20	24.5×10^{-4}	
2-Hydroxymethylpyridine	0.700	9.63×10^{-4}	$4.3 \pm 0.2 \times 10^{-4}$
2-(β-Hydroxyethyl)pyridine	0.700	8.13×10^{-4}	$2.8 \pm 0.2 \times 10^{-4}$
2-(γ-Hydroxypropyl)pyridine	0.700	7.93×10^{-4}	$2.5 \pm 0.2 \times 10^{-4}$
Benzoic acid	0.703	31.8×10^{-4}	$38 \pm 1 \times 10^{-4}$

Deuterium Isotope Measurements. Rate measurements on isomerizations of deuteriomandelaldehyde dimer (**1b**) in anhydrous pyridine at various initial concentrations of **1b** and in aqueous pyridine at various concentrations of water produced the values shown in Table V (see Figure 2). The values shown in Table I were calculated from these data.

Rate Dependence on Para Substituents (Hammett Correlation). Rate measurements in aqueous pyridine at 90° of 1.0 M (calculated as the monomer) solutions of mandelaldehyde substituted in the para position with methoxyl-, methyl-, chloro-, and trifluoromethyl groups gave the results shown in Table VI (see Figures 3 and 4).

Rate Dependence on General Acid Catalyst. Rate measurements of isomerizations of 2.0 M solutions (calculated as the monomer) of mandelaldehyde in pyridine at 90° containing varying amounts of protic species gave the results shown in Table VII (see Figure 5).

Rate Dependence on Benzamidine Concentration. Rate measurements of isomerization of 2.0 M solutions (calculated as the monomer) of mandelaldehyde in pyridine at 90° containing varying amounts of benzamidine, prepared by the method of Beggs and Spencer,[28] gave the results shown in Table VIII.[29]

Table VIII

[Benzamidine], M	k_{obsd}, sec^{-1}
0.000167	8.24×10^{-4}
0.00132	12.4×10^{-4}
0.00252	15.4×10^{-4}
0.00399	21.5×10^{-4}
0.00485	28.0×10^{-4}
0.00858	50.0×10^{-4}

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[28] B. H. Beggs and R. D. Spencer, *Anal. Chem.*, **34**, 1590 (1962).

[29] We are indebted to Mr. Chung-Lieh Wang for carrying out these measurements.

Organic Photochemistry. XI. The Photocycloaddition of Benzophenone to Conjugated Dienes[1]

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Contribution from the Dyson Perrins Laboratory, Oxford University, Oxford, England. *Received December 29, 1970*

Abstract: The photoreaction of benzophenone with several conjugated dienes leads to oxetanes. Other reaction products are those resulting from transfer of triplet excitation energy from benzophenone to the diene, and hydrogen abstraction by triplet benzophenone. For the benzophenone–2,3-dimethyl-1,3-butadiene reaction, a mechanism of oxetane formation is proposed which involves attack of excited triplet benzophenone on a ground state diene molecule. The rate constant for this cycloaddition is $\sim 1.5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ which thus competes inefficiently with the transfer of triplet excitation energy from benzophenone to diene. The further conversion of the photoproducts, under acidic conditions into 1,1-diphenylbutadienes and then into phenylindenes, is described.

Recently there has been considerable interest in the photocycloaddition reactions of carbonyl compounds to olefinic derivatives[2] to yield oxetanes.[3] It was originally proposed that reaction involved attack of the triplet (n,π^*) state of the ketone to give the most stable biradical, which subsequently cyclized to the oxetane.[3b] Ketones with lowest (π,π^*) triplet states appeared unreactive.[4] However, for aliphatic ketones, it has since been shown that reaction may proceed *via* a complex involving the (n,π^*) singlet state of the ketone,[5] or by both singlet and triplet mechanisms si-

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[1] Part X: J. A. Barltrop and D. Giles, *J. Chem. Soc. C*, 105 (1969).

[2] (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience, New York, N. Y., 1967, p 111; (c) S. Toki and H. Sakurai, *Bull. Chem. Soc. Jap.*, **40**, 2885 (1967); (d) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 598 (1967); (e) S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, **34**, 1181 (1969).

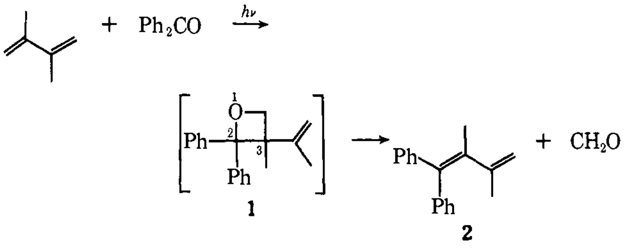
[3] (a) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); (b) G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **78**, 876 (1956).

[4] (a) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (b) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

multaneously.[6] For aromatic ketones, intersystem crossing from the singlet to the triplet manifold is much faster than for aliphatic ketones, and the singlet state photocycloaddition competes much less favorably with the intersystem crossing step. Thus the cycloaddition reactions of benzophenone[2d] and benzaldehyde[7] to olefins have been observed to arise solely from the triplet state. Fluorenone, in which the intersystem crossing rate is slower than in benzophenone, does show cycloaddition to ketenimines by both singlet and triplet mechanisms.[8]

Limitations may be imposed upon the triplet mechanism for oxetane formation by the relative energies of the triplet states of the ketone and olefinic derivative. If the olefin has a triplet energy approximately equal to, or less than, that of the ketone, then triplet–triplet energy transfer may occur in competition with (or to the exclusion of) oxetane formation.[9] It is because of their low triplet energies (54–60 kcal/mol) that conjugated dienes have been used successfully to quench the excited triplet state of ketones[10] (typical triplet energies: acetone, 77 kcal/mol;[10] acetophenone, 74 kcal/mol;[11] benzophenone, 69 kcal/mol[11]).

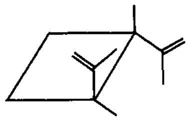
Saltiel, Coates, and Dauben[12] have reported that, in the photoreaction between benzophenone and 2,3-dimethyl-1,3-butadiene, adduct formation occurred in competition with triplet energy transfer. To explain the formation of the adduct **2** they postulated an oxetane intermediate **1**, which was not isolated. These workers also proposed a mechanism of formation of the oxetane involving attack of a diene triplet on a ground state benzophenone molecule. Such a mechanism was almost unprecedented for a simple photocycloaddition reaction, although some evidence has been put forward to suggest that the cycloaddition of acetone to dimethyl maleate or fumarate may involve interaction of excited unsaturated ester and ground state acetone,[13a] and the cycloaddition of benzophenone to an olefin (anethole) may involve attack of the excited olefin on ground state ketone.[13b]



We now wish to report a reinvestigation of the benzophenone–2,3-dimethyl-1,3-butadiene reaction, in which the oxetane has been isolated. We also present evidence to suggest that the mechanism of the photocycloaddition is not as outlined above, but that it involves attack of triplet benzophenone on a ground state diene molecule. The cycloaddition seems to be a general photochemical process, since oxetanes were also obtained by irradiating benzophenone with 1,3-butadiene, 2-methyl-1,3-butadiene, and 2,5-dimethyl-2,4-hexadiene.

Results

A mixture of benzophenone and 2,3-dimethyl-1,3-butadiene in benzene was irradiated with a medium pressure mercury arc, using a Pyrex filter under conditions similar to those of the previous workers.[12] Chromatography yielded three fractions, the first of which consisted of dimers of the 2,3-dimethyl-1,3-butadiene (21%): preparative vpc allowed the isolation of the major isomer, which was assigned the structure *trans*-1,2-diisopropenyl-1,2-dimethylcyclobutane (**3**). The second compound to be eluted was the oxetane **1** (38–40%). It showed strong absorption in the infrared at 990 cm^{-1}, in the characteristic oxetane region.[14] The nmr spectrum showed ten aromatic protons, an AB pair of doublets at τ 5.08 and 5.84 (J = 5.6 Hz) which correspond to the protons on the oxetane C_4 atom, a $=CH_2$ multiplet at 5.15–5.18, and methyl singlets at 8.45 and 8.76. The mass spectrum of **1** showed a weak molecular ion; the main fragments arose from fission across the oxetane ring in both possible directions. Further elution of the column yielded benzpinacol (23%), a commonly observed product in photoreactions of benzophenone in solutions containing molecules with readily abstractable hydrogen atoms (*e.g.*, isopropyl alcohol,[15] benzhydrol[16]).



3

In view of the failure of the previous workers to isolate **1**, its stability seemed of interest. The oxetane was unchanged after heating at 100° in a sealed tube and was stable on neutral alumina (the column material of Saltiel, Coates, and Dauben[12]). It was eluted as a single peak on vpc at 150° (fluorosilicone oil column), although it appeared to be readily decomposed to give another peak by traces of acid on the inlet heater or column. It therefore seems that the previous failure to isolate an oxetane must have been due to traces of acid, present either in the reaction product or introduced on work-up. Treatment of **1** with dilute aqueous perchloric acid (6×10^{-3} M) in methanol gave 2,3-dimethyl-1,1-diphenyl-1,3-butadiene (**2**) in 92% isolated yield.

With stronger perchloric acid (10^{-2} to 10^{-1} M) the oxetane gave a mixture of **2** with another compound, which was the sole product (isolated in 91% yield)

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(5) (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968); (b) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968).

(6) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968).

(7) N. C. Yang, R. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967).

(8) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).

(9) (a) See D. R. Arnold, *Advan. Photochem.*, **6**, 332 (1968); (b) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **88**, 3765 (1966); (c) L. A. Singer and P. D. Bartlett, *Tetrahedron Lett.*, 1887 (1964).

(10) For references, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(11) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

(12) J. Saltiel, R. M. Coates, and W. G. Dauben, *ibid.*, **88**, 2745 (1966).

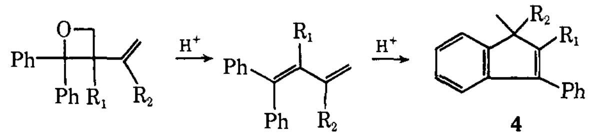
(13) (a) E. S. Albone, *ibid.*, **90**, 4663 (1968); (b) H. Nozaki, I. Otani, R. Noyori, and M. Kawanisi, *Tetrahedron*, **24**, 2183 (1968).

(14) G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

(15) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(16) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

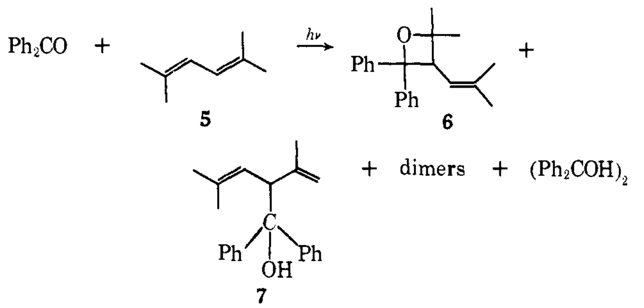
when the oxetane **1** was treated with 1 *M* perchloric acid; it was identified as 1,1,2-trimethyl-3-phenylindene (**4**). The indene appears to arise from the diene

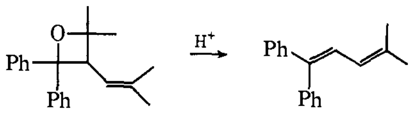


1, $R_1 = R_2 =$ Me
9, $R_1 =$ Me; $R_2 =$ H
16, $R_1 = R_2 =$ H
2, $R_1 = R_2 =$ Me
13, $R_1 =$ Me; $R_2 =$ H
15, $R_1 =$ H; $R_2 =$ Me
17, $R_1 = R_2 =$ H
4, $R_1 = R_2 =$ Me
14, $R_1 =$ Me; $R_2 =$ H

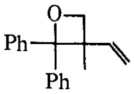
2, from which it was also prepared by treatment with 1 *M* perchloric acid. Analogously, 1,1-diphenyl-1,3-butadiene has been reported to cyclize quantitatively to 1-methyl-3-phenylindene in the presence of concentrated sulfuric acid.[17]

Irradiation of benzophenone with 2,5-dimethyl-2,4-hexadiene (**5**) under similar conditions appeared to give four products. These were (i) a complex mixture of hydrocarbon dimers, (ii) an oxetane **6**, (iii) an unsaturated alcohol **7** arising by excited benzophenone hydrogen abstraction from the dimethylhexadiene, followed by radical recombination, and (iv) benzpinacol. The nmr spectrum of the oxetane **6** showed four nonequivalent methyl groups, ten aromatic protons, and a pair of doublets at 5.01 and 6.02 (J = 10.7 Hz) assigned to the vinyl proton and oxetane C_3 proton, respectively. Its mass spectrum was also consistent with this structure. Final evidence for the structure **6** was obtained by treatment with dilute perchloric acid, which gave 1,1-dimethyl-4,4-diphenyl-1,3-butadiene (**8**) in 92% yield.





An irradiation of benzophenone and isoprene in benzene gave three main fractions: (i) isoprene dimers, of which three were isolated by preparative vpc and identified as *trans*-1,2-dimethyl-1,2-divinylcyclobutane, *trans*-2-isopropenyl-1-methyl-1-vinylcyclobutane, and *trans*-1,2-diisopropenylcyclobutane, (ii) an oxetane **9**, and (iii) benzpinacol. The oxetane was identified by spectral data. In particular, the nmr spectrum showed the structure as **9** rather than as any of the other three oxetane structures **10**, **11**, and **12**. Further evidence for the structure as **9** was provided by treatment of the oxetane with dilute perchloric acid to yield 2-methyl-1,1-diphenyl-1,3-butadiene (**13**) and, with stronger acid, 1,2-dimethyl-3-phenylindene (**14**).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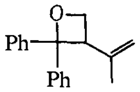
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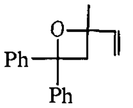
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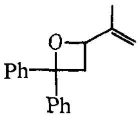
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The failure to isolate **10** would be poor evidence that it was not formed. A much better criterion would be to treat the crude photoproduct with dilute acid which would have the effect of converting the oxetanes **9** and **10**, respectively, into 2-methyl- and 3-methyl-1,1-diphenyl-1,3-butadiene. The presence of significant amounts of the latter isomer in the former can be detected by nmr, for their methyl signals would appear at τ 8.09 and 8.54. In fact, no absorption of τ 8.54 could be observed. We can therefore conclude that the oxetane isomer **10** can, at best, be present only in very small amounts.

Irradiation of benzophenone with 1,3-butadiene gave, in addition to butadiene dimers, a polymer, 2,2-diphenyl-3-vinyloxetane (**16**). Again, confirmation of the structure was provided by treatment of the oxetane with dilute perchloric acid, to give 1,1-diphenyl-1,3-butadiene (**17**) with properties identical with those of a synthesized sample.

Mechanistic Discussion. In our investigations, the irradiations of benzophenone with the conjugated dienes were conducted in Pyrex apparatus using benzene solvent. Under these conditions, only the $^1(n,\pi^*)$ state of benzophenone is excited. Uv spectra showed no evidence for a ground state complex of benzophenone with diene. Rapid intersystem crossing ($k > 5 \times 10^9$ sec^{-1} [16]) gives the $^3(n,\pi^*)$ state ($E_T \sim 69$ kcal/mol) from which energy is efficiently transferred to the conjugated diene (E_T = 54–60 kcal/mol) to yield the diene $^3(\pi,\pi^*)$ state. Any of these three states (benzophenone excited singlet or triplet, diene excited triplet) could, in principle, be responsible for the photocycloaddition.

The singlet excited state of the diene is unlikely to be involved in the photocycloaddition on the grounds, first, that it is energetically inaccessible: the singlet excitation energy of 1,3-butadiene has been suggested to lie at 112 kcal/mol (256 nm) or somewhat higher[18] and that of 2,3-dimethyl-1,3-butadiene is unlikely to be very different, but in Pyrex apparatus, the available excitation energy is less than 100 kcal/mol. More powerful evidence against the involvement of the singlet excited state comes from the failure both by Saltiel, *et al.*, and the present authors to detect 1,2-dimethylcyclobutene as a product[19] of the reaction.

Any kinetic studies of the benzophenone–2,3-dimethyl-1,3-butadiene cycloaddition require a method of following the reaction. Although the oxetane **1** could be eluted from a vpc column, the size of the peak was not entirely reproducible, being extremely sensitive to traces of acid on the column or inlet heater.

A solution to this problem was found in treating the photoproduct with dilute perchloric acid, thereby transforming the oxetane into the diene **2** and the indene **4**, both readily estimated by glc. The conversions **1** → **2** and **2** → **4** proceed virtually quantitatively (products *isolated* in yields >90%, and no other peaks observable on glc) so that measuring the amounts of **2** and **4** permits the calculation of the quantity of oxetane formed.

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(17) V. Bertoli and P. H. Plesch, *Chem. Commun.*, 625 (1966).

(18) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).

(19) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962).

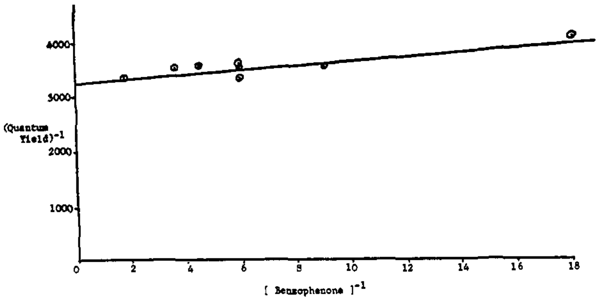

Figure 1. Plot of ϕ_{ox}^{-1} *vs.* [benzophenone]$^{-1}$ for photocycloaddition of benzophenone to 2,3-dimethylbutadiene (0.44 *M* in benzene).

In order to investigate the quantum yield of oxetane formation as a function of the concentration of reactants, Pyrex tubes containing known concentrations of benzophenone and 2,3-dimethyl-1,3-butadiene in benzene were irradiated in a merry-go-round reactor. After irradiation, the photoproduct in each tube was treated with dilute perchloric acid, and subjected to glc analysis. The quantum yields[20] of oxetane formation were obtained by benzophenone-benzhydrol actinometry.[16] Plots were thus obtained for reciprocal of quantum yield (ϕ_{ox}^{-1}) against reciprocal of benzophenone concentration (B^{-1}) (Figure 1), and reciprocal of quantum yield against reciprocal of 2,3-dimethyl-1,3-butadiene (D^{-1}) (Figure 2).

Saltiel, Coates, and Dauben[12] proposed a mechanism of formation of the diene **2** (*via* oxetane **1**) involving attack of the triplet excited diene on ground state benzophenone. Their pictorial scheme can be formalized as Scheme I, where B, B_1, and B_3 are ground state, first excited singlet state, and lowest triplet state, respectively, of benzophenone; D and D_3 are ground and triplet states, respectively, of diene. Excitation of benzophenone is followed by intersystem crossing to the triplet state (eq 1); pseudounimolecular deactivation of the triplet can occur (eq 2); the diene quenches the triplet state of benzophenone by triplet-triplet energy transfer (eq 3). The triplet diene can react with ground state benzophenone to give oxetane (eq 4), or with ground state diene, to give diene dimers (eq 5). Alternatively, the triplet may undergo deactivation to the ground state (eq 6). Steady-state treatment on the species B_1, B_3, and D_3 leads to the expression

Scheme I

$$\begin{array}{lr}
B \xrightarrow{I} B_1 & \text{Excitation} \\
B_1 \xrightarrow{k_1} B_3 & (1) \\
B_3 \xrightarrow{k_2} B & (2) \\
B_3 + D \xrightarrow{k_3} B + D_3 & (3) \\
D_3 + B \xrightarrow{k_4} \text{oxetane} & (4) \\
D_3 + D \xrightarrow{k_5} \text{dimers} & (5) \\
D_3 \xrightarrow{k_6} D & (6)
\end{array}$$

$$1/\phi_{ox} = \frac{k_2 + k_3D}{k_3D}\left(1 + \frac{k_5D + k_6}{k_4B}\right) \qquad \text{(i)}$$

where ϕ_{ox} is the quantum yield of oxetane. It is possible to simplify eq i with a knowledge of some of the rate constants involved. k_2, the rate of radiationless decay of the benzophenone triplet, is thought to be about 3 × 10^5 sec^{-1} in benzene at room temperature.[16] The rate of quenching of triplet benzophenone by conjugated dienes, k_3, is thought to be diffusion controlled (in benzene, 5 × 10^9 M^{-1} sec^{-1}).[21] Therefore, at concentrations of diene greater than 10^{-2} *M*, $k_2 \ll k_3D$ and eq i simplifies to

$$1/\phi_{ox} = 1 + \left(\frac{k_5D + k_6}{k_4}\right)\frac{1}{B} \qquad \text{(ii)}$$

If the postulated mechanism holds, then at a fixed concentration of diene, a plot of ($1/\phi_{ox}$) against ($1/B$) would be expected to be linear, with an intercept of 1.

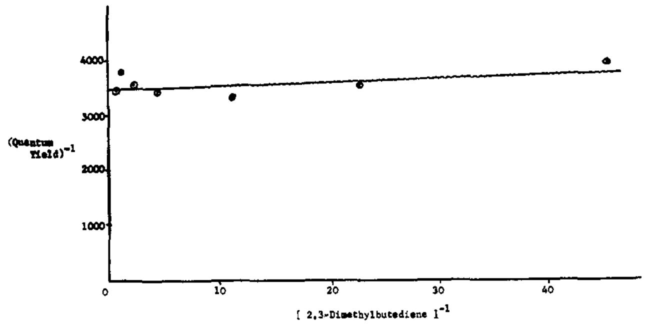

Figure 2. Plot of ϕ_{ox}^{-1} *vs.* [diene]$^{-1}$ for photocycloaddition of benzophenone to 2,3-dimethylbutadiene (0.11 *M* benzophenone in benzene).

Figure 1 is a plot of reciprocal of quantum yield ($1/\phi_{ox}$) against reciprocal of benzophenone concentration (B^{-1}). Although the low quantum yield of the photoreaction means that very small concentrations of photoproduct had to be determined (and thus the scatter on the points is rather large: precision ±10%), the results do show that the plot of $1/\phi_{ox}$ against B^{-1} does not have an intercept of 1. "Least squares" analysis gave an intercept of 3290 ± 350 and a slope of 37 ± 50. The results cannot fit eq ii derived from Scheme I, and it would seem that attack of the triplet diene on ground state benzophenone is not the process leading to oxetane formation.

Many cases of oxetane formation are known in which attack of triplet excited benzophenone occurs on a ground state olefin molecule.[2a,c,d] It seemed a reasonable possibility that this kind of mechanism might also hold for the benzophenone-diene reaction, as set out in Scheme II. Thus, triplet benzophenone would still be quenched by ground state diene (eq 3a), but this step would be in competition with attack of triplet benzophenone on ground state diene to give oxetane (eq 7). Again, the triplet diene could react with ground state diene to dimerize, or undergo radiationless deactivation.

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[20] The lamps used have a dominant broad emission in the range 270–320 nm. Under the condition of the experiment, the benzophenone absorbed light of λ 280–320 nm and a little of λ 366 nm. Since benzophenone is used both as substrate and actinometer, the quantum yield calculations should be unaffected by the polychromatic character of the light except in the unlikely event that the photoaddition reaction is wavelength dependent.

[21] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

Scheme II

$$\mathrm{B} \xrightarrow{h\nu} \mathrm{B_1} \qquad \text{Excitation}$$

$$\mathrm{B_1} \xrightarrow{k_1} \mathrm{B_3} \qquad (1a)$$

$$\mathrm{B_3} \xrightarrow{k_2} \mathrm{B} \qquad (2a)$$

$$\mathrm{B_3} + \mathrm{D} \xrightarrow{k_3} \mathrm{B} + \mathrm{D_3} \qquad (3a)$$

$$\mathrm{B_3} + \mathrm{D} \xrightarrow{k_7} \text{oxetane} \qquad (7)$$

Steady-state treatment on B_1 and B_3 gives the expression

$$1/\phi_{\mathrm{ox}} = \frac{k_3 + k_7}{k_7} + \frac{k_2}{k_7}\left(\frac{1}{D}\right) \qquad \text{(iii)}$$

Scheme II predicts that the reciprocal of quantum yield should be independent of any function of the benzophenone concentration. This is in agreement with the observed results: the slightly positive slope of the observed plot may be a result of decreases in light absorption of the tubes with decreased benzophenone concentration. Particularly relevant in this respect is that the tube containing the lowest concentration of benzophenone is the only one deviating from the average quantum yield by greater than ±4%.

If Scheme II does represent the mechanism of the cycloaddition, the low quantum yield has significance: a value $\phi = 0.0003$ was found at a concentration of diene $\simeq 0.5\ M$. The use of this fact in eq iii together with the values mentioned earlier for k_2 and k_3 gives an approximate value for k_7, the rate step of the cycloaddition reaction.[22]

$$k_7 = k_3\phi = 1.5 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$$

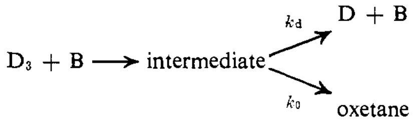
Two steps which have been omitted from the above kinetic schemes deserve mention. The first

$$\mathrm{B_1} \xrightarrow{k_8} \mathrm{B} \qquad (8)$$

radiationless decay of the benzophenone excited singlet state to ground state, is omitted because it is unimportant: the high triplet quantum yield of benzophenone (1.00[23]) shows eq 8 is not a significant pathway for deactivation of the excited singlet. Even its inclusion at a rate one-tenth of that of intersystem crossing merely increases the intercept and slope of eq ii and iii by a constant factor (10%).

The second step omitted is hydrogen abstraction from the diene by excited triplet benzophenone. This does occur, as evidenced by the yields of benzpinacol found, and competes for removal of triplet benzophenone. The rate constants for such hydrogen abstractions are small, however ($2\text{–}9 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ [24,25]), in comparison with the triplet energy transfer term, k_3. They do not alter the essential dependences of the kinetic scheme.

It is possible to envisage a situation where the distinction we have been able to draw between Schemes I and II would become invalid. Such a situation could occur if a triplet diene molecule were to attack a ground state benzophenone molecule to give "reversible" intermediate formation, and this intermediate partitioned between ground state reactants and formation of oxetane. This additional pathway for deactivation of the diene triplet could then lead to an intercept of greater than 1 for the plot of $1/\phi_{\mathrm{ox}}$ *vs.* B^{-1}. Steady-state analysis including such a step in Scheme I would necessitate (from Figure 1) that $k_d/k_0 \simeq 3300$. If this mechanism were to hold, the interpretation of the very low quantum yield of oxetane formation is that attack of the diene triplet on a benzophenone molecule produces an intermediate (possibly a biradical) which then leads efficiently, and by an unknown mechanism, to deactivation of the diene triplet. Biradical intermediates which decay to ground state reactants have been proposed in several photochemical processes,[2c,26] but there does not seem to be a precedent for such a high k_d/k_0 ratio as would be required in the present example. Nevertheless, such a mechanism cannot be rejected *a priori.*



However, we have been able to provide additional strong evidence against attack of a triplet diene on a ground state benzophenone molecule as the mechanism of oxetane formation, by an experiment using 2-acetonaphthone as a reaction sensitizer. The results are given in Table I.

Table I. Products from Irradiations of Benzophenone and 2-Acetonaphthone in the Presence of 2,3-Dimethylbutadiene (2,3-D)

Irradiations[a]	Relative amounts of oxetane (**1**)	Relative amounts of diene dimers
Ph_2CO + 2,3-D	1.00	1.0
Ph_2CO + 2,3-D + 2-acetonaphthone[b]	0.08 ± 0.03	3.7 ± 0.8
2,3-D + 2-acetonaphthone[c]	0.00	4.5 ± 0.8

[a] Irradiations were conducted in Pyrex tubes inside the Rayonet reactor using 300-nm output lamps, under conditions such that each tube absorbed equal amounts of light. Concentrations used were 0.44 *M* 2,3-D, 0.11 *M* Ph_2CO, and 0.11 *M* 2-acetonaphthone in benzene solvent. [b] The 2-acetonaphthone was calculated to absorb 90–95% of the incident light, when used as sensitizer. [c] Tlc and glc failed to show any other reaction products.

The sensitized experiment is an attempt to excite selectively the diene to its triplet state. 2-Acetonaphthone has a triplet energy of 59 kcal/mol[27] and when used as sensitizer should therefore transfer triplet energy rapidly to diene molecules, yet only at a very slow rate to benzophenone since energy transfer to the latter would be ~10 kcal/mol endothermic. The reaction products bear out the fact that diene triplets are formed in the

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(22) We cannot exclude the possibility that attack of triplet benzophenone on diene gives cycloaddition *via* an intermediate (*e.g.*, a Schenck-type biradical) which partitions between decay to ground state reactants and formation of oxetane, in which case the rate constant for intermediate formation may be greater than that calculated for Scheme II.

(23) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(24) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **83**, 528 (1963).

(25) P. J. Wagner, *Mol. Photochem.*, **1**, 71 (1969).

(26) (a) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968); (b) J. A. Barltrop and J. D. Coyle, *Chem. Commun.*, 1081 (1969); (c) P. de Mayo, A. A. Nicolson, and M. F. Tchir, *Can. J. Chem.*, **47**, 711 (1969); (d) P. J. Wagner and D. J. Bucheck, *ibid.*, **47**, 713 (1969); (e) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969); (f) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

(27) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

sensitized irradiation, because diene dimers are produced in a greater yield than in the direct benzophenone–2,3-dimethylbutadiene reaction.[28] However, the product distribution of the sensitized reaction suggests that these diene triplets are not responsible for oxetane formation: thus the oxetane yield, far from being that of the direct reaction, is reduced to an amount explicable by direct competitive light absorption by the benzophenone present. Therefore, attack by triplet diene on benzophenone to give an oxetane (*via* a rapidly decaying intermediate) cannot be the process involved in the photocycloaddition.

There remains the possibility that reaction occurs *via* the singlet excited state of benzophenone. No such reactions have been reported, but the low quantum yield in the present case would not require an unreasonably high bimolecular rate constant for the photocycloaddition, as can be seen from consideration of Scheme

Scheme III

$$\mathrm{B} \xrightarrow{h\nu} \mathrm{B_1}$$

$$\mathrm{B_1} \xrightarrow{k_1} \mathrm{B_3} \qquad (1)$$

$$\mathrm{B_1} \xrightarrow{k_8} \mathrm{B} \qquad (8)$$

$$\mathrm{B_1} + \mathrm{D} \xrightarrow{k_9} \text{oxetane} \qquad (9)$$

III. Steady-state approximation on B_1 gives

$$1/\phi_{\text{ox}} = 1 + \frac{k_1 + k_8}{k_9}\left(\frac{1}{D}\right) \qquad \text{(iv)}$$

as $1/\phi_{\text{ox}} = 3300$ at $D \simeq 0.5\ M$, and assuming $k_8 \ll k_1$ and that $k_1 = 5 \times 10^9\ \text{sec}^{-1}$

$$k_9 \simeq 3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$$

This value of k_9 is three orders of magnitude below diffusion controlled, and would not be prohibitively high for a singlet rate constant of photocycloaddition. For example, singlet rate constants of photocycloaddition of acetone to 1-methoxy-1-butene[6] and *trans*-1,2-dicyanoethylene[5a] have been estimated at 2×10^8 and 1×10^8 M^{-1} sec^{-1}, respectively. Scheme III also predicts that the reciprocal of quantum yield of oxetane formation should be independent of benzophenone concentration.

The mechanisms involving singlet or triplet excited benzophenone attack on ground state diene can be distinguished. Consider the variation of reciprocal of quantum yield with reciprocal of diene concentration.

Scheme II, involving triplet benzophenone and using the value of k_7 ($1.5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$) calculated from the first experiment, with the values of k_2 and k_3 mentioned earlier, predicts (*vide* eq iii)

$$1/\phi_{\text{ox}} = 3300 + 0.2D^{-1} \qquad \text{(v)}$$

Scheme III, involving singlet benzophenone and using the calculated value of k_9 ($3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$), assuming $k_1 = 5 \times 10^9\ \text{sec}^{-1}$, gives (*vide* eq iv)

$$1/\phi_{\text{ox}} = 1 + 1600D^{-1} \qquad \text{(vi)}$$

Figure 2 is a plot of $1/\phi_{\text{ox}}$ against (D^{-1}). It shows that $1/\phi_{\text{ox}}$ is independent of D^{-1}. "Least-squares" analysis gave an intercept of 3490 (± 350) and a slope of 7.7 (± 10), *i.e.*

$$1/\phi_{\text{ox}} = 3490 + 7.7D^{-1} \qquad \text{(vii)}$$

It is clear that there is a complete lack of correspondence between the experimentally derived equation (vii) and the predicted equation (vi) suggesting that Scheme III (singlet mechanism) is not the reaction sequence implicated in the photocycloaddition (unless to a very minor extent). On the other hand, given the uncertainties in the values of some of the rate constants used (particularly k_2) and the experimental errors in our own work, there is reasonable agreement between eq v and vii.

We therefore conclude that the photocycloaddition of benzophenone to 2,3-dimethyl-1,3-butadiene occurs by a mechanism involving attack of triplet excited benzophenone on ground state diene, with a rate constant of about $1.5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, and that this process is in competition with the diffusion controlled quenching of triplet benzophenone by the conjugated diene.

Experimental Section

Irradiation. Preparative irradiations were conducted in a cylindrical reactor (200 ml) fitted with a Pyrex probe and a 450-W Hanovia medium-pressure Hg arc, after deoxygenation with purified nitrogen. Comparative irradiations were performed in Pyrex tubes inside a Rayonet reactor equipped with a merry-go-round and 300-nm lamps.

Glc. Gas-liquid chromatography was conducted on columns designated as follows: ODP, 20% di-2-cyanoethyl ether on Embacel; TCEP, 20% tris-1,2,3-(2-cyanoethoxy)propane on Embacel; QF1, 15% fluorosilicone fluid (FS 1265, Perkin-Elmer) on Anakrom 40/50 A (Analabs Inc.); L, 15% Apiezon L grease on Chromosorb P; DDP, 15% di-*n*-decyl phthalate on Embacel.

Irradiation of Benzophenone with 2,3-Dimethylbuta-1,3-diene. A solution of 2,3-dimethylbutadiene (4.35 g) and benzophenone (12 g) in benzene (180 ml) was deoxygenated and irradiated for 91 hr. Solvent was removed by rotary evaporation to leave a viscous liquid (14.5 g), of which 4.0 g was chromatographed on silica gel (100 g) and eluted with 5% ether–petroleum ether (bp 30–60°). The first fraction (105 mg, 21%) was tentatively identified as a mixture of the diene dimers, *cis*- and ***trans*-1,2-diisopropenyl-1,2-dimethylcyclobutane,** in the (nmr) ratio 1:4. (*Anal.* Calcd for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.5; H, 12.0.) Nmr (60 and 100 MHz, CCl_4) showed τ 5.15–5.4 (4 H, complex, $=CH_2$), 7.7–9.2 (complex, cyclobutane CH_2CH_2), 8.25 and 8.43 (6 H, each a singlet, ratio 4:1, $CH_3C=$), 8.88 and 9.03 (6 H, each a singlet, ratio 4:1, *tert*-CH_3),; $\nu_{\max}$ (film) 3090 w ($=CH_2$), 2980 s (CH), 1635 s (C=C), 1450 s, 1378 s (CH_3), 895 s cm^{-1} ($=CH_2$). Preparative glc (4-m ODP, 65°) of this mixture allowed the isolation of a single product, assigned the structure *trans*-1,2-diisopropenyl-1,2-dimethylcyclobutane (**3**): nmr (CCl_4) τ 5.18 and 5.28 (4 H, each a broad singlet), 7.7–9.0 (4 H, complex), 8.25 (6 H, singlet), 8.88 (6 H, singlet); $\nu_{\max}$ (film) 3090 w ($=CH_2$), 2970 s, 2860 s (CH), 1635 s (C=C), 1450 s, 1375 s (CH_3), 1240 m, 1085 m, 895 s cm^{-1} ($=CH_2$). Analytical glc showed the product as a single peak on two columns (4-m ODP, 65°, and 4-m TCEP, 73°). The next fraction (600 mg, 38% on converted diene, 40% on unrecovered benzophenone), a colorless low-melting solid, was identified as **3-isopropenyl-3-methyl-2,2-diphenyloxetane (1).** (*Anal.* Calcd for $C_{19}H_{20}O$: C, 86.3; H, 7.6. Found: C, 86.0; H, 7.6.) Nmr (CCl_4) showed τ 2.5–2.9 (10 H, complex, aromatic), 5.08 and 5.84 (each 1 H, doublet, J = 5.6 Hz, oxetane ring CH_2), 5.15–5.18 (2 H, multiplet, $=CH_2$), 8.45 (3 H, singlet, $CH_3C=$), 8.76 (3 H, singlet, CH_3C); $\nu_{\max}$ (film) 3070 m ($=CH_2$), 2980 s, 2880 s (CH), 1635 m (C=C), 1600 m, 1500 s (C_6H_5), 1380 m (CH_3), 992 s (oxetane), 900 s ($=CH_2$), 865 s, 850 s, 710 s cm^{-1} (C_6H_5); mass spectrum 264 (0.3, parent), 234 (1.5), 219 (5), 183 (90), 182 (40, Ph_2CO), 105 (90), 82 (100, C_6H_{10}), 77 (52), 67 (45).

Elution with 10% ether–petroleum ether gave successively benzophenone and benzpinacol (230 mg, 23%).

Treatment of Oxetane (1) with Acid. 3-Isopropenyl-3-methyl-2,2-diphenyloxetane (250 mg), dissolved in methanol (20 ml) and aqueous perchloric acid (20 μl of 60%), was left overnight at room temperature, then rotary evaporated, and adsorbed on silica gel

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[28] A very similar variation in diene dimer quantum yield has been observed previously for isoprene dimerization, using benzophenone and 2-acetonaphthone as sensitizers; see R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(20 g). Elution with 2% ether-petroleum ether gave 2,3-dimethyl-1,1-diphenyl-1,3-butadiene (**2**) (204 mg, 92%). (*Anal.* Calcd for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.7.) Nmr (CCl_4) showed τ 2.7–3.0 (10 H, complex, aromatic), 5.18 (2 H, multiplet, $=CH_2$), 8.11 (3 H, singlet, $Ph_2C=C(C\mathit{H}_3)$), 8.31 (3 H, broad singlet, $C(C\mathit{H}_3)=CH_2$); ν_{max} (film) 3070 s ($=CH_2$), 1635 m ($C=C$), 1600 m, 1498 s (C_6H_5), 1445 s, 1375 m (CH_3), 900 s ($=CH_2$), 760 s, 700 s cm^{-1} (C_6H_5); mass spectrum 235 (12), 234 (66, parent), 220 (18), 219 (100), 204 (30), 203 (15), 202 (12), 157 (12), 142 (10). The product gave a single peak on glc (QF1, 150°).

3-Isopropenyl-3-methyl-2,2-diphenyloxetane (43 mg) was dissolved in methanol (1 ml) and aqueous perchloric acid (0.1 ml, 60%) and left overnight. Work-up gave a viscous liquid (39 mg, 91%) identified as **1,1,2-trimethyl-3-phenylindene (4)**. (*Anal.* Calcd for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 91.9; H, 7.9.) Nmr (CCl_4) showed τ 2.6–2.9 (9 H, complex, aromatic), 8.06 (3 H, singlet, $=CCH_3$), 8.70 (6 H, singlet, $C(CH_3)_2$); ν_{max} (film) 1600 m, 1500 m (C_6H_5), 784 s (4 adjacent aromatic CH), 760 s, 704 s (C_6H_5), 660 s cm^{-1}; mass spectrum 235 (23), 234 (100, parent), 220 (21), 219 (92), 204 (30), 203 (26), 202 (24), 141 (9). The product gave a single peak on glc (QF1, 150°).

Irradiation of Benzophenone with 2,5-Dimethyl-2,4-hexadiene. A solution of benzophenone (6.0 g) and 2,5-dimethyl-2,4-hexadiene (5 ml) in benzene (185 ml) was deoxygenated and irradiated for 21 hr, then rotary evaporated. A 3.0-g sample of the residue was chromatographed on silica gel (150 g). Elution with 4% ether-petroleum ether gave first a mixture of 2,5-dimethylhexadiene dimers (102 mg) (*Anal.* Calcd for $C_{16}H_{28}$: C, 87.2; H, 12.8. Found: C, 87.6; H, 12.5), followed by a mixture (561 mg) of two photoproducts and some benzophenone. The mixture (400 mg) was separated by tlc (2.5% ether-petroleum ether four times) to give **2,2-dimethyl-3-(2-methylprop-1-enyl)-4,4-diphenyloxetane (6)** (113 mg). (*Anal.* Calcd for $C_{21}H_{24}O$: C, 86.3; H, 8.3. Found: C, 86.0; H, 8.3.) Nmr (CCl_4) showed τ 2.6–2.9 (10 H, complex, aromatic), 5.01 (1 H, broad doublet, J = 10.7 Hz, $=CH$), 6.02 (1 H, sharp doublet, J = 10.7 Hz, C(3)-H of oxetane ring), 8.24 and 8.30 (each 3 H, singlet, $=C(CH_3)_2$), 8.62 and 8.80 (each 3 H, singlet, $(CH_3)_2CO$); ν_{max} (film) 3060 m, 3030 m, 2970 s, 2920 s ($=CH$ and CH), 1660 w ($C=C$), 1600 m, 1496 s (C_6H_5), 1452 s, 1380 s (CH_3), 1005 s (oxetane), 890 s, 775 s, 750 s, 705 s cm^{-1} (C_6H_5); mass spectrum 234 (25, $C_{18}H_{18}$), 219 (30), 182 (35, Ph_2CO), 110 (100, C_8H_{14}), 109 (50), 105 (55), 95 (55), 77 (37). The other component (42 mg) separated by tlc was assigned the structure **2-isopropenyl-4-methyl-1,1-diphenylpent-3-en-1-ol (7)**. (*Anal.* Calcd for $C_{21}H_{24}O$: C, 86.3; H, 8.3. Found: C, 85.9; H, 8.0.) Nmr (CCl_4) showed τ 2.5–2.9 (10 H, complex, aromatic), 4.65 (1 H, slightly split doublet, J = 9 Hz, $=C(3)$-H), 5.27 (2 H, doublet, $=CH_2$), 6.06 (1 H, doublet, J = 9 Hz, C_2H), 7.30 (1 H, broad singlet, D_2O exchangeable, OH), 8.40 and 8.46 (each 3 H, singlet, $=C(CH_3)_2$), 8.60 (3 H, singlet, isopropenyl $-CH_3$); ν_{max} (Nujol) 3525 m (OH), 3060 m ($=CH$), 1660 m ($C=C$), 1600 w, 1500 m (C_6H_5), 1380 s (CH_3), 1050 m (C-OH), 900 m ($=CH_2$), 750 s, 695 s cm^{-1} (C_6H_5); mass spectrum 292 (missing, parent), 275 (0.5), 183 (100, Ph_2COH), 182 (15), 110 (65, C_8H_{14}), 105 (82), 95 (12), 77 (42). Further elution of the column with 10% ether-petroleum ether yielded benzpinacol (240 mg).

Treatment of Oxetane 6 with Acid. 2,2-Dimethyl-3-(2-methylprop-1-enyl)-4,4-diphenyloxetane (50 mg) in methanol (5 ml) was treated with perchloric acid (10 μl, 60%) and left for 8 hr. Work-up gave 1,1-dimethyl-4,4-diphenyl-1,3-butadiene (**8**) (37 mg, 92%): nmr (CCl_4) τ 2.7–2.9 (10 H, complex, aromatic), 3.22 (1 H, sharp doublet, J = 11 Hz, $Ph_2C=C\mathit{H}$), 4.15 (1 H, broad doublet, J = 11 Hz, $C\mathit{H}=CMe_2$), 8.11 and 8.23 (each 3 H, singlet, $=C(CH_3)_2$); ν_{max} (film) 3050 s, 2960 s, 2920 s ($=CH$ and CH), 1640 w ($C=C$), 1600 m, 1496 s (C_6H_5), 1380 m (CH_3), 770 s, 735 s, 702 s cm^{-1} (C_6H_5); mass spectrum 234 (80, parent), 219 (100), 204 (30), 203 (14), 202 (11), 191 (15). The product gave a single peak on glc (QF1, 150°).

Irradiation of Benzophenone with 2-Methyl-1,3-butadiene. A solution of 2-methyl-1,3-butadiene (3.4 g) and benzophenone (9.1 g) in benzene (165 ml) was deoxygenated, and irradiated for 64 hr. Uv spectra showed that 83% of the benzophenone had reacted.

Solvent was removed from a fraction of the product (50 ml) and the residue subjected to column chromatography on silica gel (100 g). Elution with 2% ether-petroleum ether gave a band (630 mg) as a mixture of three compounds, not properly separated by further column chromatography.

Tlc (10% ether-petroleum ether) of this fraction gave, in order of elution, three isolated bands. **2-Methyl-1,1-diphenyl-1,3-butadiene (13)** (19 mg) had nmr (CCl_4) τ 2.7–2.9 (10 H, complex, aromatic), 3.37 (1 H, double doublet, J = 11 and 17 Hz, $-C\mathit{H}=CH_2$), 4.72 and 4.95 (each 1 H, broad doublet, J = 17 and 11 Hz, respectively, $=CH_2$), 8.07 (3 H, singlet, CH_3); ν_{max} (film) 3080 m ($=CH_2$), 1640 w ($C=C$), 1380 m (CH_3), 998 m, 908 s ($-CH=CH_2$), 765 s, 700 s cm^{-1} (C_6H_5); glc (QF1, 150°) showed a single peak. The second band was identified as **3-methyl-2,2-diphenyl-3-vinyloxetane (9)** (191 mg): nmr (60 and 100 MHz, CCl_4) τ 2.5–2.9 (10 H, complex, aromatic), 4.00 (1 H, double doublet, J = 10 and 18 Hz, $-C\mathit{H}=CH_2$), 4.92, 5.13 (2 H, multiplet, $=CH_2$), 5.53 and 5.78 (each 1 H, doublet, J = 5.3 Hz, CH_2O), 8.80 (3 H, singlet, CH_3); ν_{max} (film) 3070 w ($=CH$), 1640 m ($C=C$), 1600 m, 1500 s, 765 s (C_6H_5), 1380 m (CH_3), 995 s (oxetane), 920 s cm^{-1} ($-CH=CH_2$); mass spectrum 250 (0.5, parent), 220 (1.5, loss of CH_2O), 205 (3), 183 (52), 182 (40, Ph_2CO), 105 (100), 77 (48), 68 (35, C_5H_8), 67 (17). The third band was benzophenone (31 mg).

Treatment of 3-Methyl-2,2-diphenyl-3-vinyloxetane with Acid. The oxetane (120 mg) dissolved in methanol (10 ml) and perchloric acid (0.1 ml, 60%) was left overnight. After work-up, tlc (2.5% ether-petroleum ether two times) gave two narrowly separated bands: the first was 2-methyl-1,1-diphenylbutadiene (35 mg) with properties as described above, and the second was identified as **1,2-dimethyl-3-phenylindene (14)** (36 mg) (*Anal.* Calcd for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.3; H, 7.8). Nmr (60 and 100 MHz, CCl_4) showed τ 2.65, 2.90 (9 H, complex, aromatic), 6.72 (1 H, quartet, J = 7.5 Hz, $C\mathit{H}(CH_3)$), 7.96 (3 H, singlet, $CH_3C=$), 8.64 (3 H, doublet, J = 7.5 Hz, $CH(C\mathit{H}_3)$); ν_{max} (film) 1600 m, 1500 s (C_6H_5), 780 s (4 adjacent aromatic C–H), 765 s, 704 s cm^{-1} (C_6H_5). The product gave a single peak on glc (QF1, 150°).

Preparation of 3-Methyl-1,1-diphenyl-1,3-butadiene (15). The Grignard complex from methallyl chloride (8.85 g) and magnesium turnings (2.3 g-atoms) in dry ether (200 ml) was prepared. Benzophenone (9.1 g) in ether (100 ml) was added to the Grignard reagent slowly, with stirring. The solution was refluxed for 2 hr, cooled, and poured into saturated aqueous ammonium chloride (200 ml). Isolation with ether gave **3-methyl-1,1-diphenylbut-3-en-1-ol** (10.2 g, 86%): nmr (60 MHz, CCl_4) τ 2.5–2.9 (10 H, complex, aromatic), 5.15–5.3 (2 H, doublet, $=CH_2$), 7.00 (2 H, singlet, CH_2), 7.40 (1 H, singlet, OH), 8.65 (3 H, singlet, CH_3); ν_{max} (film) 3520 s (OH), 3080 s, 910 s ($=CH_2$), 1655 s ($C=C$), 1060 s, 750 s, 700 s cm^{-1} (C_6H_5).

The above alcohol (2.35 g) was dehydrated by refluxing for 2 hr with phosphorus oxychloride (2.5 ml) and pyridine (25 ml). The product was rotary evaporated, and column chromatography on silica gel (100 g) eluting with 4% ether-petroleum ether gave **3-methyl-1,1-diphenyl-1,3-butadiene** (1.60 g, 74%). (*Anal.* Calcd for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.4; H, 7.5.) Nmr (60 MHz, CCl_4) showed τ 2.7–2.9 (10 H, complex, aromatic), 3.40 (1 H, singlet, C(2)-H), 5.04 (2 H, multiplet, $=CH_2$), 8.53 (3 H, slightly split singlet, CH_3); ν_{max} (film) 3080 s, 904 s ($=CH_2$), 1380 m (CH_3), 765 s, 700 s cm^{-1} (C_6H_5).

Irradiation of Benzophenone with 1,3-Butadiene. A solution of benzophenone (12 g) and butadiene (10 g) in benzene (170 ml) was irradiated for 72 hr. Tlc showed two main products, plus polymer and some unreacted benzophenone (30% by uv spectra). Glc (15% DDP, 85°, and 4-m ODP, 65°) of the product showed the presence of the four butadiene dimers *cis*- and *trans*-1,2-divinylcyclobutane, 4-vinylcyclohexene, and *cis,cis*-1,5-cyclooctadiene. The other major product could not be isolated pure by repeated column chromatography of a rotary evaporated fraction (50 ml) on silica gel (100 g), eluting with 3% ether-petroleum ether, but a fraction (600 mg) rich in the photoproduct was obtained. Tlc (10% ether-petroleum ether) allowed the separation of a colorless liquid (190 mg) assigned the structure **2,2-diphenyl-3-vinyloxetane (16)**. (*Anal.* Calcd for $C_{17}H_{16}O$: C, 86.5; H, 6.8. Found: C, 86.8; H, 6.5.) Nmr (CCl_4) showed τ 2.6–2.9 (10 H, complex, aromatic), 5.30 (1 H, double doublet, J = 5.7 and 8.6 Hz), 5.54 (1 H, double doublet, J = 5.7 and 7.1 Hz, oxetane ring CH_2O), 4.42 (1 H, double doublet, J = 9.3, 10, and 17 Hz, $-C\mathit{H}=CH_2$), 4.92 and 5.06 (each 1 H, double doublet, J = 17 and 2, 10 and 2 Hz, respectively, $=CH_2$), 5.86 (1 H, broad quartet, oxetane ring C(3)-H); ν_{max} (film) 3080 s, 920 s ($-CH=CH_2$), 1640 w ($C=C$), 990 s (oxetane), 755 s, 700 s cm^{-1} (C_6H_5).

The above oxetane (40 mg) was treated with perchloric acid (0.005 ml) and methanol (5 ml). Work-up gave 1,1-diphenyl-1,3-butadiene (28 mg) having ir and nmr spectra identical with those of an authentic sample, prepared as described below.

Preparation of 1,1-Diphenyl-1,3-butadiene (17). The route and conditions used were similar to those for the preparation of 3-methyl-1,1-diphenylbutadiene. To the Grignard complex from allyl chloride (15 g) and magnesium (4.6 g-atoms) in ether (350 ml) was

Table II

Tube	Weight of benzophenone, g	(Molarity of benzophenone)$^{-1}$	Ratio (R) $C_{18}H_{18}$/hexadecane	Corrected ratio R	$1/\phi$
1	0.199	18.2	0.0094	0.0097	4040
2	0.399	9.1	0.0107	0.0111	3530
3	0.600	6.07	0.0108	0.0114	3440
4	0.801	4.55	0.0106	0.0109	3570
5	1.001	3.64	0.0109	0.0110	3550
6	1.999	1.82	0.0116	0.0116	3380
7	0.600	6.07	0.0108	0.0111	3530
8	0.600	6.07	0.0114	0.0117	3350

added benzophenone (18.2 g) in ether (100 ml). Work-up gave 1,1-diphenylbut-3-en-1-ol (19.8 g, 89%) as a colorless oil: nmr (60 MHz, CCl_4) τ 2.5–2.9 (10 H, complex, aromatic), 4.0–5.1 (3 H, complex, -CH=CH_2), 7.01 (2 H, doublet, J = 6.5 Hz, CH_2), 7.64 (1 H, singlet, OH); ν_{max} (film) 3500 s (OH), 3070 s (=CH_2), 1055 s (C-O), 995 s, 910 s (-CH=CH_2), 760 s, 700 s cm^{-1} (C_6H_5). The alcohol (1.0 g) was dehydrated with phosphorus oxychloride (1.0 g) and pyridine (15 ml). The product was purified by column chromatography (100 g of silica gel) to give 1,1-diphenyl-1,3-butadiene (710 mg, 77%). (*Anal.* Calcd for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 92.8; H, 6.7.) Nmr (CCl_4) showed τ 2.6–2.9 (10 H, complex, aromatic), 3.35 (1 H, doublet, J = 10.5 Hz, C(2)-H), 3.62 (1 H, double double doublet, J = 9, 10.5, and 15.5 Hz, -C*H*=CH_2), 4.62 and 4.92 (each 1 H, double doublet, J = 15.5 and 9 Hz, respectively, =CH_2); ν_{max} (film) 3080 s (=CH_2), 1620 m (C=C), 1450 s, 995 s, 910 s (-CH=CH_2), 770 s, 700 s cm^{-1} (C_6H_5).

Variation of Quantum Yield of Oxetane Formation with Benzophenone Concentration. Solutions containing various weights of benzophenone (as below) and 2,3-dimethyl-1,3-butadiene (1 ml) were made up to 20 ml with Analar benzene, and poured into the calibrated Pyrex tubes. The tubes were deoxygenated by nitrogen bubbling for 15 min, sealed, and irradiated in the Rayonet merry-go-round for 30 hr using 16 × 300 nm lamps. The temperature of the tubes during irradiation was approximately 34°. At the end of the irradiation, 2-ml samples were taken from each tube and to each was added *n*-hexadecane (0.05 ml) as internal standard and methanol (1 ml), followed by perchloric acid (0.01 ml, 60%). After standing for 10 hr, tlc showed the oxetane had been completely converted into the diphenyldiene and indene derivative. Glc (15% L, 250°) allowed these (unresolved) product peaks to be determined relative to the internal standard: the ratios (R) were measured by cutting out and weighing the peaks. A calibration experiment of weighed solutions of *n*-hexadecane against the $C_{18}H_{18}$ hydrocarbons gave K = 0.92($C_{18}H_{18}$/*n*-hexadecane). A correction for the nonuniformity of the tubes was applied to the observed ratios.

A separate experiment, under the same conditions, irradiating a deoxygenated (three freeze-pump-thaw cycles at 10^{-2} mm) solution of benzophenone (0.1 *M*) and benzhydrol (0.1 *M*) in benzene gave 0.033 mol of benzophenone converted in 30 min of irradiation (with already running lamps). Assuming constant lamp intensity and a quantum yield for the reaction of 0.66,[16] this corresponds to a conversion of 0.10 mol of benzophenone/hr with a quantum yield of reaction of 1.

From the observed glc ratios (R), the number of moles of oxetane (assumed equal to the number of moles of $C_{18}H_{18}$ hydrocarbons) (Table II) produced per hour could be calculated

$$= \frac{R}{30}\,\frac{0.92 \times 19.4}{234} = 0.00254R$$

Hence the quantum yield in a single tube = (no. of moles of benzophenone leading to oxetane, per hour)/(no. of moles of benzophenone consumed per hour, when ϕ = 1) = 0.0254R.

Variation of Quantum Yield of Oxetane Formation with 2,3-Dimethylbutadiene Concentration. Solutions containing various molarities of 2,3-dimethylbutadiene (as below) and benzophenone (400 mg, 0.11 *M*) were made up to 20 ml with benzene, and irradiated exactly as in the previous experiment for 30 hr. After irradiation, samples (2 ml) were taken from each tube, and to each was added methanol (1 ml), perchloric acid (0.01 ml, 60%), and 2-acetonaphthone (9 mg) as internal standard. Glc (QF1, 150°) allowed the sum of the areas of the diphenyldiene (R_t 6.4) and indene-derivative peaks (R_t 12.6) to be measured relative to that of the internal standard (R_t 19). This ratio (R) could be converted to a weight of product using the determined glc conversion factor, K = 1.09($C_{18}H_{18}$/2-acetonaphthone). The quantum yields were then determined by the method in the previous experiment, from the expression ϕ = 0.0070R, where R is the corrected glc area ratio (Table III).

Table III

Tube	Volume of diene, ml	(Molarity diene)$^{-1}$	Ratio (R) $C_{18}H_{18}$/2-acetonaphthone	Corrected ratio R	$1/\phi$
1	0.05	45.3	0.0350 0.0352	0.0360 0.0362	3970
2	0.1	22.6	0.0391	0.0405	3530
3	0.2	11.3	0.0411	0.0431	3320
4	0.5	4.53	0.0404	0.0418	3430
5	1.0	2.26	0.0392	0.0397	3610
6	2.0	1.13	0.0378 0.0377	0.0378 0.0377	3790
7	4.0	0.57	0.0401	0.0413	3470

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