Irradiation of Naphthalene in the Presence of 2,3-Dimethyl-1,3-butadiene and 1,2-Dimethylcyclobutene. A solution of 1.38 g (0.011 mole) of naphthalene and 1.0 g (0.012 mole) of 2,3-dimethyl-1,3-butadiene in 135 ml of benzene was irradiated under standard conditions using a Pyrex filter. Samples were removed periodically and were analyzed by glpc (20% TCEP). At the end of 21 hr of irradiation, no 1,2-dimethylcyclobutene could be detected, although there was a slight drop in diene concentration. The irradiation was interrupted, and 1,2-dimethylcyclobutene was added, and the irradiation was continued for another 20 hr. No conversion of the cyclobutene to the diene occurred. Again there was a slight drop in the concentration of diene.

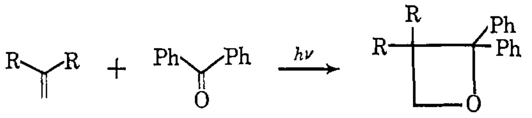
Photochemical Cycloaddition of 2,3-Dimethyl-1,3-butadiene and 1,2-Dimethylcyclobutene to Benzophenone[1,2]

Jack Saltiel,[3] Robert M. Coates,[4] and William G. Dauben

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received February 10, 1966*

Abstract: Conditions are described which permit adduct formation between benzophenone and 2,3-dimethyl-1,3-butadiene although triplet excitation transfer to the diene remains the major path of energy dissipation from the benzophenone triplets. A mechanism is proposed which involves addition of diene triplets to benzophenone in its ground state.

Studies of the photochemistry of mixtures of ketones or aldehydes and olefinic or acetylenic compounds have shown that two major reaction pathways are available. The first involves cycloaddition of the carbonyl moiety to a carbon–carbon double or triple bond[5–8] (eq 1 and 2) and the second involves triplet excitation transfer from the ketone to the hydrocarbon substrate with subsequent reaction of the substrate. Typical examples of the latter path are the sensitized *cis–trans* isomerization of the stilbenes,[9] the sensitized valence isomerization of 1,3-cyclooctadiene[10] and 1,1′-bicyclohexenyl,[11] and the sensitized dimerization of 1,3-butadiene and isoprene.[12]



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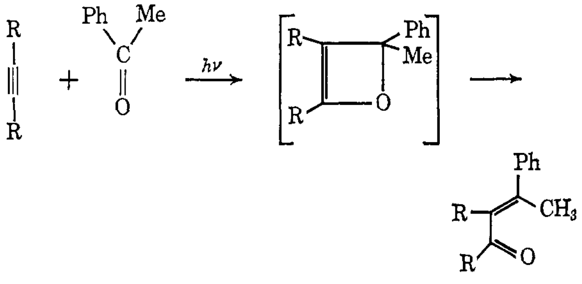

(2)

Two generalizations have been made concerning cycloaddition.[8,13] The first is that only carbonyl compounds whose lowest triplet state is of the n → π* type react (*e.g.*, 2-acetonaphthone whose lowest triplet is of the π → π* type is found to be inert), and the second is that cycloaddition occurs provided triplet excitation transfer from the ketone to the unsaturated substrate is inefficient. In agreement with this second restriction it is found that the most suitable substrates for cycloaddition are compounds which have *isolated* double or triple bonds. In general, the spectroscopic triplet states of these latter unsaturated compounds lie higher in energy than the triplet states of compounds containing the carbonyl moiety,[14] and only the relatively inefficient nonvertical excitation transfer may occur in these systems. An example of the latter process is the benzophenone-sensitized *cis–trans* isomerization of 2-pentene.[9,15]

The favored mechanism for known cycloadditions is shown for reaction 1 in eq 3–5. The process involves attack by the electron-deficient oxygen of the n → π* triplet state of the ketone upon the ground state of the unsaturated hydrocarbon. The products can be accounted for if it is assumed that the attack occurs at the position which will lead to the formation of the most stable diradical.[5,16]

As part of a broad program on the mechanism of photochemically induced valence isomerisms of 1,3-butadiene to 1,2-cyclobutenes, an investigation was initiated to see if a triplet state was an essential intermediate.[11] In the course of this work it was found that

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(1) For the previous paper in this series, see W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966).

(2) This work was supported in part by PHS Grant No. 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(3) National Science Foundation Postdoctoral Fellow, 1964.

(4) National Science Foundation Cooperative Fellow, 1960–1963.

(5) G. Büchi, C. G. Inman, and E. S. Lipinski, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

(6) G. Büchi, J. T. Kopron, E. Koller, and D. Rosenthal, *ibid.*, **78**, 876 (1956).

(7) H. E. Zimmerman and L. Craft, *Tetrahedron Letters*, 2131 (1964); D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, 2137 (1964).

(8) D. A. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964).

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

(10) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

(11) See ref 1.

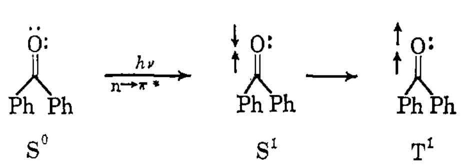
(12) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(13) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

(14) Compare 82 kcal/mole for ethylene (D. F. Evans, *J. Chem. Soc.*, 1735 (1960)) with 74 kcal/mole for acetophenone (W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5437 (1964)).

(15) G. S. Hammond, N. J. Turro, and P. A. Leermarkers, *J. Chem. Phys.*, **66**, 1144 (1962).

(16) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).



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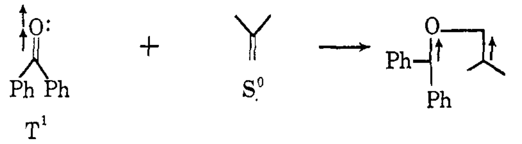

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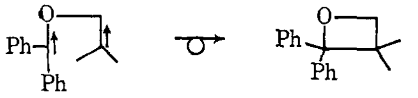
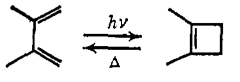


(5)

under certain conditions cycloaddition could be obtained in systems where the major deactivation of the carbonyl compound was triplet excitation transfer to the unsaturated hydrocarbon substrate. The present investigation is concerned with results pertaining to the cycloaddition reaction.

Results and Discussion

Direct ultraviolet irradiation readily converts 2,3-dimethyl-1,3-butadiene (**1**) to 1,2-dimethyl-1-cyclobutene (**2**) [eq 6].[11,17,18] This conversion could not be effected

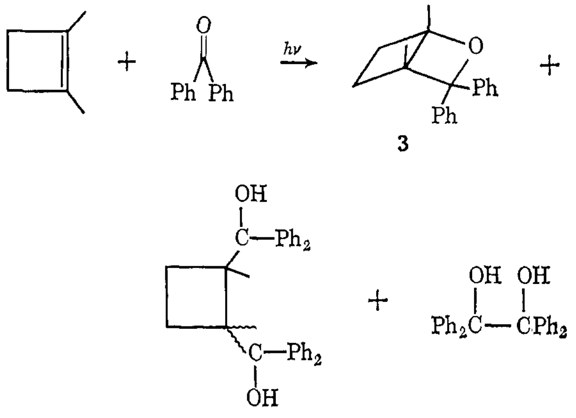


1 **2**

(6)

when a benzene solution of **1** containing benzophenone, in amounts varying from 0.5 to 2 equiv, was irradiated under a helium atmosphere with a Pyrex-filtered ultraviolet light. Under such irradiation conditions all the incident radiation is absorbed by the benzophenone and the expected course of events would be intersystem crossing to form the triplet state of benzophenone followed by very efficient triplet transfer from benzophenone to the 1,3-diene.[12,19] This scheme was verified for the system under consideration by studying the benzophenone–benzhydrol photoreduction[20] in the presence of 2,3-dimethyl-1,3-butadiene. It was found that by making a benzene solution which was 0.13 *M* in benzophenone and 1.3 *M* in benzhydrol also 2.7 *M* in diene, the half-life of the benzophenone was increased from 15 min to 23 hr. This quenching of the photoreduction is consistent with the expected, essentially quantitative, triplet excitation transfer from benzophenone to **1**.

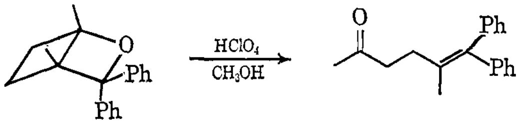
The progress of several irradiations of benzophenone in the presence of **1** was followed by glpc. It was found that after lengthy periods of irradiation, for example 140 hr with a 450-w Hanovia lamp, as much as 40–60% of the diene was consumed. Since **2** could not be detected throughout the course of each irradiation, the possibility that **1** might be slowly converted to **2** which in turn reacts very rapidly with benzophenone triplets was investigated. 1,2-Dimethylcyclobutene was irradiated in *n*-pentane in the presence of benzophenone. The disappearance of benzophenone was followed by ultraviolet analysis and that of 1,2-dimethylcyclobutene by glpc. It was found that both compounds were consumed rapidly and that no **1** was detected as a product. The course of this last photoreaction is shown in eq 7. The oxetane **3** was formed in 48%



3 **4**

(7)

yield, benzpinacol in 31% yield, and **4** in trace amounts.[21] Upon treatment with acid, **3** was converted quantitatively to the ketone **5** (eq 8) which was

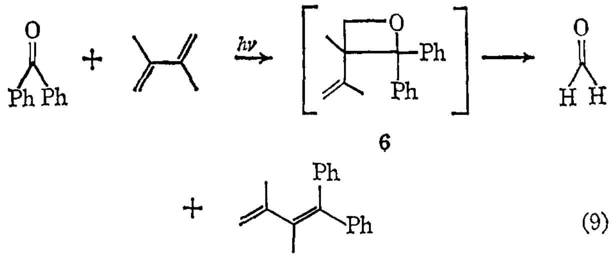


3 **5**

(8)

characterized as its 2,4-dinitrophenylhydrazone. Interestingly, **3** and **5** have practically identical mass spectra.

Analysis for products in the 2,3-dimethyl-1,3-butadiene–benzophenone system showed that the reaction proceeded slowly but cleanly, as shown in eq 9. 1,1-Diphenyl-2,3-dimethyl-1,3-butadiene (**7**) was isolated in yield as high as 28% and no ether product could be



6 **7**

(9)

detected. It is not known, however, whether **7** is the primary photoproduct. By analogy with the normal cycloaddition reaction (eq 1 and 2) the oxetane **6** is a likely intermediate. Of special interest is the fact that **3** is not a product in this reaction. The absence of **3** in the present reaction (**9**) taken together with the finding that the diene is an efficient quencher of the benzophenone triplet *establishes conclusively that the conversion of the diene to the cyclobutene (eq 6) does not proceed by way of the triplet state.* Furthermore, the absence of **7** in the reaction of **2** with benzophenone

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[17] R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962); R. Srinivasan, *ibid.*, **85**, 4045 (1963).

[18] K. J. Crowley, *Tetrahedron*, **21**, 1001 (1964).

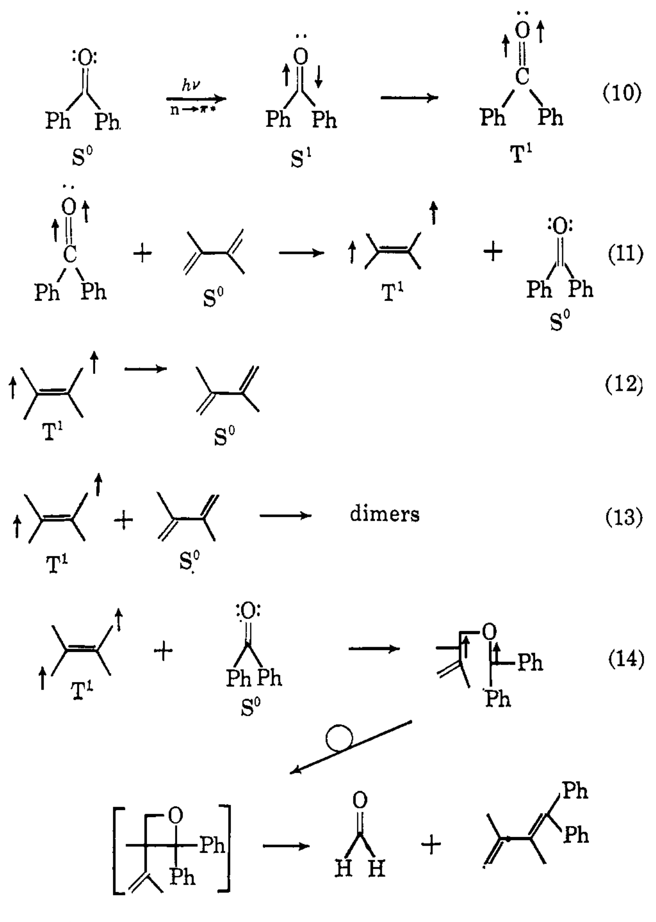
[19] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

[20] G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

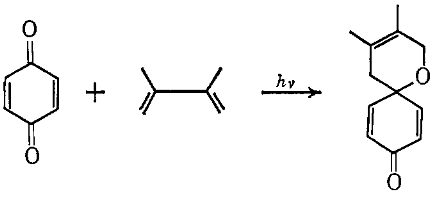
[21] The formation of benzhydrol radicals in this medium is probably due to hydrogen abstraction of *n*-pentane by benzophenone triplets: C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964).

(eq 7) shows that this cyclobutene does not revert to the diene **1** in the presence of a triplet sensitizer.[22]

The fact that previous attempts to detect reactions analogous to eq 9 have been unsuccessful[8] seems to have mechanistic significance. The crucial difference between the present experiments and those carried out by other investigators[8,12] is probably to be found in the ratios of diene to ketone employed. In the past, the carbonyl compounds were irradiated in the presence of a great excess of unsaturated hydrocarbon substrate. Under such conditions the frequency of encounters between diene triplets and diene ground-state molecules is much greater than between diene triplets and ketone ground-state molecules with the result that diene dimers are the only observed products. In the present experiments benzophenone was present in equivalent or larger quantity than the diene so that ground-state benzophenone could compete effectively with ground-state diene for diene triplets. The mechanism which best accounts for all the available results is shown in eq 10–14.



Although benzophenone with a triplet excitation energy of 68.7 kcal/mole[12] would be expected to transfer triplet excitation energy to *s-cis*-2,3-dimethyl-1,3-butadiene ($E_T \sim$ 54 kcal/mole[23]) as well as to *s-trans*-2,3-dimethyl-1,3-butadiene ($E_T \sim$ 60 kcal/mole[23]) at equal, diffusion-controlled rates, the results do not require the intermediacy of *cis* diene triplets.[24] This fact might indicate either that in this system *cisoid* diene triplets are shorter lived or that they are less reactive than *transoid* diene triplets. In any case, it seems of great relevance that the photoreaction of 1,4-benzoquinone[25] with **1** proceeds as shown in eq 15. The triplet excitation energy of 1,4-benzoquinone is



(15)

8

about 50 kcal/mole[9] and if triplet excitation transfer from 1,4-benzoquinone to **1** is a key step in reaction 15, then transfer leading to *cisoid* triplets should predominate.[22] Thus the formation of products **8** is entirely consistent with the mechanism proposed for reaction 9.

Experimental Section[26]

General Irradiation Procedure. All irradiations (unless otherwise noted) were performed using a 450-w Hanovia mercury lamp (Type 679A 36) and a Hanovia quartz immersion probe (Type 19434). The cylindrical irradiation flask into which the probe was inserted was of 130- or 450-ml volume and contained two side arms. One arm was fitted with a small condenser capped by a mercury exit seal; the other arm was fitted with a serum cap to permit removal of aliquots. All reaction mixtures were outgassed by flushing thoroughly with a stream of helium and the gas flow was continued during the irradiation. The solution was stirred with a magnetic stirring apparatus.

All pentane used in irradiation experiments was washed twice with concentrated sulfuric acid, stirred for 12 hr with 30% fuming sulfuric acid, washed with several portions of water and several portions of aqueous sodium hydroxide, passed through basic alumina, and distilled from phosphorus pentoxide.

Irradiation of 1,2-Dimethylcyclobutene in the Presence of Benzophenone. A solution of 3.6 ml (2.34 g, 28.5 mmoles) of 2,3-dimethyl-1,3-butadiene (Fluka A.G., Chemische Fabrik, 90% monomer) in 350 ml of irradiation pentane was irradiated under the standard conditions for 6.5 hr and then through a Vycor filter for 10.5 hr. The progress of the reaction was followed by glpc analysis using a Hy-Fi Model 600-C Aerograph apparatus equipped with a 5 ft × 1/8 in. column packed with 20% TCEP on Chromosorb P (60–80 mesh). At the end of the irradiation period no diene remained in the reaction mixture. The conversion to 1,2-dimethylcyclobutene was practically quantitative; a second product was produced in less than 2% yield and it was not investigated.

To the reaction mixture there was added 6.5 g (35.7 mmoles) of benzophenone (Matheson Coleman and Bell, reagent grade) and the irradiation was continued for 12.5 hr using a Pyrex filter. At the end of this period glpc analysis revealed that about 3% of the 1,2-dimethylcyclobutene remained and the concentration of the unknown minor photoproduct from the diene remained unaltered. Also, the analysis showed no starting diene either at the beginning or at the end of the irradiation period. The benzpinacol which precipitated during the irradiation was filtered and recrystallized, yielding 2.0 g (31%).

The pentane filtrate was concentrated and the 7 g of yellow oily residue, which was shown by infrared analysis to contain no

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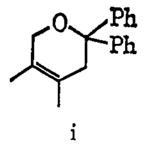
[22] A sensitized equilibration has been observed between 1,1′-bicyclohexenyl and its valence isomer and the details will be reported separately.

[23] G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

[24] It is unlikely that the undetected ether i would be the precursor of the diene 7.



i

[25] J. A. Barltrop and B. Hesp, *Proc. Chem. Soc.*, 195 (1964); *J. Chem. Soc.*, 5182 (1965).

[26] All elemental analyses by the Microanalytical Laboratory, College of Chemistry, University of California. All mass spectral analyses by the Mass Spectral Laboratory, College of Chemistry, University of California, using a Consolidated 103 spectrometer.

benzophenone, was chromatographed on 170 g of basic Woelm alumina (activity III). Elution with 170 ml of *n*-pentane yielded 0.5 g of an oily residue which from its physical and spectral properties appeared to be a mixture of dimeric and polymeric hydrocarbons (no aromatic materials). Further elution with *n*-pentane yielded 3.6 g (48%) of the white, crystalline oxetane **3**. The material was recrystallized from ethanol, mp 112.1–112.9°. The infrared spectrum of the material in carbon tetrachloride showed the following strong maxima (μ): 3.43, 6.94, 8.51, 10.17, 10.98, and 14.19. The nmr spectrum in carbon tetrachloride showed the following bands: τ 8.80 (singlet, 3 H), 8.68 (singlet, 3 H), 7.4–8.4 (multiplet, 4 H), and 2.5–3.1 (multiplet, 10 H). The mass spectrum showed a parent peak at 264, a base peak at M − 221, and prominent peaks at M − 57, M − 73, M − 97, M − 99, M − 121, M − 136, M − 159, and M − 173.

Anal. Calcd for $C_{19}H_{20}O$ (264.35): C, 86.32; H, 7.63. Found: C, 86.04; H, 7.44.

Further elution with 100 ml of benzene yielded **4**, a yellow oil. The material crystallized from ethanol as white needles, yield 0.375 g. A portion of the solid **4** was recrystallized from ethanol, mp 159.8–160.4°. The infrared spectrum of the material in chloroform showed the following strong maxima (μ): 2.81, 3.28, 3.38, 6.71, 6.95, 8.61, 9.40, 9.58, 9.68, 13.99, and 14.22. The nmr spectrum in chloroform-*d* showed the following bands: τ 8.7 (multiplet), 7.5–8.6 (multiplet), 7.44 (singlet), and 2.8 (multiplet). The integration was not reliable since the signals were weak even though a saturated solution was used. The mass spectrum showed no parent peak, but a base peak was present at 135 mass units and a large peak was at 182 mass units.

Anal. Calcd for $C_{32}H_{32}O_2$ (448.58): C, 85.68; H, 7.19. Found: C, 85.90; H, 7.04.

Continued elution yielded a trace of another crystalline material which from its infrared spectrum appeared to be an alcohol but the substance was not investigated.

Acid Isomerization of 3 to 5. The oxetane **3** (100 mg) was dissolved in 15 ml of anhydrous methanol, 10 μl of 70% perchloric acid was added, and the solution was stirred at room temperature for 10 hr. Diethyl ether (50 ml) was added to the solution and the mixture was extracted several times with water. The ethereal layer was dried, and the ether was removed under reduced pressure on a rotary evaporator to yield **5** as an oil which could not be crystallized. The infrared spectrum in carbon tetrachloride showed the following strong maxima (μ): 3.27, 3.43, 5.82, 6.24, 6.71, 6.94, 7.38, and 14.26. The mass spectrum of the material was, except for small changes in relative peak intensities, identical with that of starting oxetane **3**. The 2,4-dinitrophenylhydrazone was prepared, mp 133.0–135.7°.

Anal. Calcd for $C_{25}H_{24}O_4N_4$ (444.47): C, 67.55; H, 5.44; N, 12.61. Found: C, 67.40; H, 5.28; N, 12.76.

Irradiation of 2,3-Dimethyl-1,3-butadiene in the Presence of Benzophenone. A solution of 3.75 ml (2.7 g, 33 mmoles) of 2,3-dimethyl-1,3-butadiene and 12 g (66 mmoles) of benzophenone in 450 ml of benzene (which had been washed for two 12-hr periods with concentrated sulfuric acid and distilled) was irradiated in the standard fashion using a Pyrex filter. Samples were periodically removed and analyzed for diene content by glpc; a low-boiling impurity in the benzene was used as the internal standard. At the end of 115 hr approximately 44% of the diene had reacted, the irradiation was stopped, and the solvent was removed under reduced pressure. The residual yellow oil (14.8 g) which showed no hydroxyl absorption in the infrared was chromatographed on 230 g of neutral Woelm alumina. The column was eluted with four 200-ml portions of *n*-pentane and three 200-ml portions of 1:1 diethyl ether–*n*-pentane. The fractions were analyzed by infrared and by glpc (5 ft × $^1/_8$ in. column of 1% Apiezon on Chromosorb Z). Fractions 6 and 7 were found to contain mainly benzophenone as the volatile product and were discarded.

Fractions 1–5 (5.8 g) containing a compound other than benzophenone were combined and rechromatographed on 100 g of Woelm neutral alumina (activity I). The column was eluted with two 100-ml portions of *n*-pentane and four 100-ml portions of 2% diethyl ether in *n*-pentane. The fractions contained 0.038, 0.418, 0.271, 0.234, 0.788, and 0.630 g, respectively. The first and the last fractions were discarded since fraction 1 appeared to contain mainly a nonvolatile material and fraction 6 was mainly benzophenone. Fractions 2 and 3 were shown to be 1,1-diphenyl-2,3-dimethyl-1,3-butadiene (**7**) (see below).

Fractions 4 and 5 were combined and rechromatographed on 44 g of Woelm neutral alumina. Elution with *n*-pentane gave 32 mg of material and two 100-ml portions of 2% diethyl ether in *n*-pentane gave 224 mg of product. The chromatography was stopped at this point and the material remaining on the column was discarded. All material eluted was shown to be the diene **7** and the total yield of the reaction was 0.913 g (12.4%). The diene solidifies in the cold but melts below room temperature. The ultraviolet spectrum showed a shoulder at 235–245 mμ (ϵ 13,700) and a strong absorption (ϵ_{205} 33,000). The infrared spectrum in CCl_4 had the following strong bands (μ): 3.28, 3.43, 6.24, 6.72, 6.95, 11.10, 11.19, and 14.30. The nmr spectrum in CCl_4 showed the following bands: τ 8.33 (multiplet, 3 H), 8.13 (singlet, 3 H), 5.23 (multiplet, 2 H), and 2.90 (multiplet, 10 H). The mass spectrum had a strong parent peak at 234 and a base peak at M − 15. A sample was purified by preparative glpc on a 10 ft × 0.5 in. diethylene glycol column.

Anal. Calcd for $C_{18}H_{18}$ (224.32): C, 92.26; H, 7.74. Found: C, 92.39; H, 7.93.

Quenching of Benzophenone–Benzhydrol Photoreduction by 2,3-Dimethyl-1,3-butadiene. A. Rate of Photoreduction. A solution of 8.0 g (44 mmoles) of benzophenone and 81 g (440 mmoles) of benzhydrol in benzene was made up to a volume of 330 ml. The solution was irradiated in the standard manner and the rate of reduction was followed by the intensity of the 253-mμ band. The half-life for the reaction varied between 13 and 15 min. During the reaction benzpinacol precipitated.

B. Quenching by 2,3-Dimethyl-1,3-butadiene. The photoreduction was repeated as above except that 10 ml (7.2 g, 89 mmoles) of diene was added. The half-life of the reaction was 23 hr.