The second portion was evaporated under vacuum to give a residue which was triturated with ether to give crystalline piperidine hydrochloride (800 mg), mp 221–227°. The ether solution was evaporated and the residue (875 mg) was sublimed three times to give acetone oxime, mp and mmp 56–58°.

To α-Methylstyrene.—The nitrosamine (5.76 g), α-methylstyrene (6.31 g), and concentrated hydrochloric acid (8 ml) were photolyzed in methanol (450 ml). The photolysate was evaporated under vacuum and then the residue was diluted with water (50 ml). The neutral and the basic fractions were extracted with ether and were worked up in an usual manner. The residue from the neutral extraction gave acetophenone oxime on crystallization from Skellysolve B, mp and mmp 56–58° (3.3 g). The mother liquor was treated with hydroxylamine hydrochloride (1 g) and sodium acetate (2 g) in ethanol to give an additional amount of the oxime (1.6 g). The total yield was 91%.

The basic extract (2.92 g) was distilled at 48–50° (0.5 mm), the infrared and nmr spectra of which were found to be superimposable with dipiperidylmethane prepared according to Knoevenagel's method.[24]

Photoaddition of N-Nitrosodimethylamine. To Cyclohexene.—The nitroso compound (7.2 g, 97.5 mmoles), cyclohexene (16.4 g, 0.2 mole), and concentrated hydrochloric acid (12 ml) were photolyzed in methanol (480 ml). The crude free base of photoadduct IIg (13.10 g, 85%) showed an infrared absorption at 1705 cm^{-1} which disappeared on oximation with hydroxylamine hydrochloride and sodium acetate in methanol. Purification was done by recrystallization from cyclohexane and finally by sublimation, mp 111–113° (lit.[25] mp 120°).

To *cis*-Cyclooctene.—The nitroso compound (3.7 g, 50 mmoles), the cyclooctene (11 g, 100 mmoles), and concentrated hydrochloric acid (8.5 ml) were photolyzed in ethanol (500 ml) for 2.5 hr. On evaporation to a small volume, the hydrochloride of the photoadduct IIb crystallized out (5.81 g) and was recrystallized from a methanol–acetone mixture, mp 204–205°. This salt was dissolved in water and was neutralized with K_2CO_3 solution to give *anti* IIb, mp 84–85°. An additional amount of the free base (3.92 g, the combined yield 97%) was isolated as an oil and was sublimed three times for analysis. The nmr spectrum of the sublimed material as well as that of the crude product, shows two methyl signals of nearly the same intensity at τ 7.77 and 7.69 indicating this is a mixture of *syn* and *anti* Ib. Chromatography of this fraction on a silicic acid column gave the *syn* isomer as the first compound to be eluted, mp 71–73°. Continuing elution gave a mixture of the isomers and then the *anti* isomer.

To 1-Methylcyclohexene.—The nitrosamine (3.74 g), 1-methylcyclohexene (5 g), and concentrated hydrochloric acid (10 ml) were photolyzed in a tetrahydrofaran (230 ml)–water (80 ml) mixture. The photolysate was set aside at room temperature overnight and evaporated under vacuum. The neutral and the basic fractions were extracted with ether and were worked up as usual. Various efforts to purify the basic fraction (746 mg) were not successful. The neutral fraction (3.85 g) was distilled at 103–105° (13 mm) to give a liquid (3.59 g) with infrared peaks at 2730 and 1710 cm^{-1} and nmr signals at τ 0.25 (1 H, triplet, J = 1 cps) 7.56 (4 H, two triplets), and 7.91 (3 H, singlet). The bishydrazone of this liquid was prepared and recrystallized from an ethyl acetate–ethanol mixture, mp 196–198°.

Anal. Calcd for $C_{19}H_{20}N_8O_8$: N, 22.94. Found: N, 23.09.

Registry No.—*syn* Ia, 10591-86-3; *anti* Ib, 10591-87-4; hydrochloride of *anti* Ib, 10591-88-5; *syn* Ic, 10591-89-6; *anti* Ic, 10591-90-9; *syn* Id, 10591-91-0; *anti* Id, 10591-92-1; *syn* Ie, 10591-93-2; *anti* Ie, 10591-94-3; *syn* If, 10591-95-4; *anti* If, 10591-96-5; *syn* IIb, 10591-97-6; *anti* IIb, 10591-98-7; hydrochloride of *anti* IIb, 10591-99-8; *syn* IIg, 10592-00-4; V, 10592-01-5; bishydrazone of 6-ketoheptanal, 10592-02-6.

Acknowledgment.—It is a pleasure to acknowledge the financial support provided by the National Research Council of Canada on the project.

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Photochemical Reactions with Phenols. I. The Photochemical Reaction of Benzophenone with 2,6-Di-*t*-butylphenol

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Received January 4, 1967

Benzophenone has been found to react photochemically with 2,6-di-*t*-butylphenol in the presence of a catalytic amount of mineral acid to yield 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane. A multistep mechanism of this new reaction has been established by either trapping or isolating all probable intermediates.

Among the representatives of light-sensitive, phenyl-substituted carbonyl compounds, benzophenone has received considerable attention. Although its photochemical transformation into benzpinacol had been observed by Ciamician and Silber[1] as early as 1900, during recent years a deeper insight into the primary steps of the photochemical reactions of benzophenone has been gained.[2–5] The mechanism of the photochemical pinacolization[6–10] as well as the scope and limitation of triplet energy transfer reactions[11–13] of benzophenone are now fairly well understood, and new reactions are sometimes predictable.

In the course of a study on the oxidation of phenols[14] the photochemical reaction of benzophenone with 2,6-di-*t*-butylphenol has been investigated since it appeared interesting and worthwhile to apply photoexcited benzophenone as a novel oxidizing agent. This paper describes a new photochemical reaction of benzophenone found in the course of this investigation.

Results

Irradiation of a methanol solution of benzophenone (I) and 2,6-di-*t*-butylphenol (II) containing a catalytic

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[1] G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1530 (1901).

[2] H. L. J. Bäckström, *Festskr. The Svedberg 1884–1944*, 45 (1944).

[3] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

[4] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1959).

[5] For a review, see G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

[6] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

[7] W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

[8] W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

[9] (a) G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1964); (b) H. W. Johnson, Jr., J. N. Pitts, Jr., and M. Burleigh, *Chem. Ind.* (London), 1493 (1964).

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[11] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

[12] V. Ermolaev and A. Terenin, *J. Chim. Phys.*, **55**, 698 (1958).

[13] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964), and other papers in this series.

[14] H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

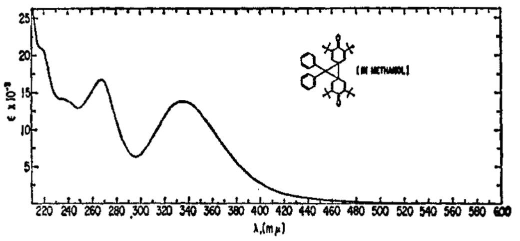
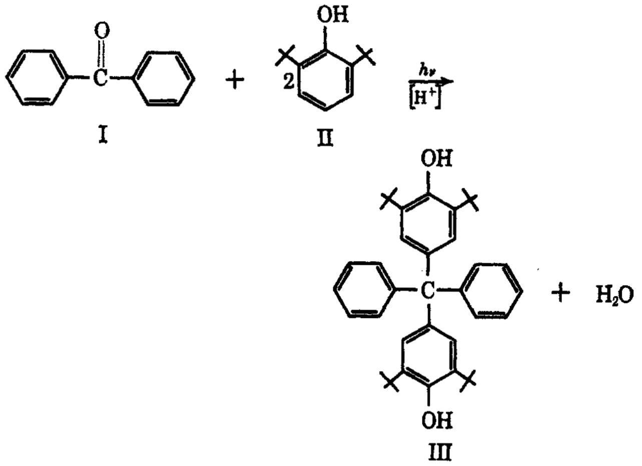


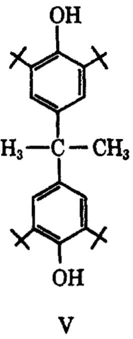
Figure 1.

amount of mineral acid, using light from a mercury lamp filtered through Pyrex glass, leads to the formation of 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (III) according to the following over-all process. The new bisphenol precipitates during the irradiation in analytically pure form in 64–68% yield.

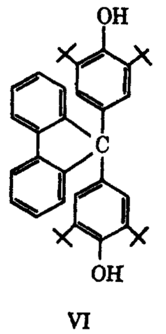


The structure of III is established by analytical and spectroscopic (infrared and nmr) data. Furthermore, oxidation of III in benzene solution with active MnO_2 produces quantitatively the new bispirodienone IV (Scheme I). Reduction of IV to give III is easily accomplished with sodium borohydride or zinc–hydrochloric acid in methanol solution. The structure of IV is fully supported by elemental analysis, molecular weight, and infrared, nmr, and ultraviolet spectra (Figure 1).

Formation of IV is of particular interest with respect to recent communications on the oxidation of the bisphenols V and VI to yield bispirodienones which have been found to be oxygen sensitive owing to an equilibrium with the corresponding biradicals.[15–17] In the case of IV, however, no evidence for a free biradical has been found. Oxidation of III with MnO_2 to give IV can be carried out in the presence of oxygen. Bispirodienone IV is thermochromic in the solid state and in solution. The compound does become paramagnetic upon heating (150°). It has not been investigated, however, whether the deep red color, developed upon heating, is associated with the appearance of the esr signal or is due to excitation from higher vibrational levels, as discussed by Grubb and Kistiakowsky[18] for the thermochromic behavior of 9-benzhydrylidene-10-anthrone.[19]

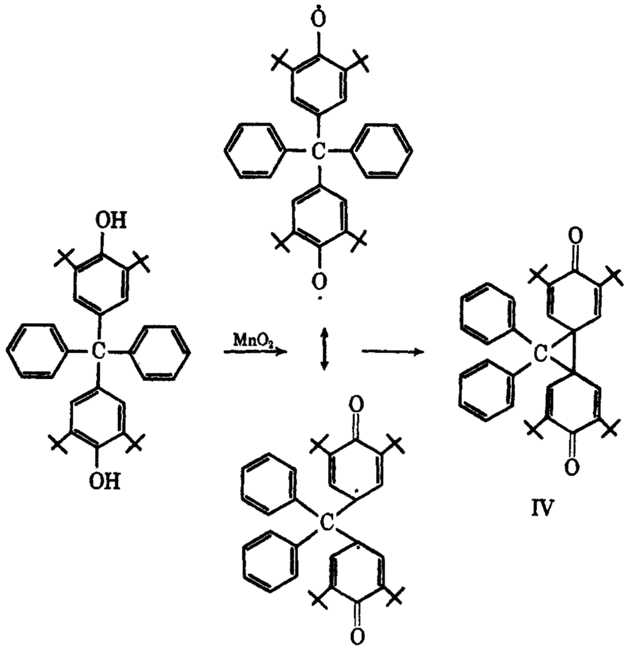


V



VI

SCHEME I



The yield of 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (III) in the photochemical reaction of 2,6-di-*t*-butylphenol is increased by using excess benzophenone. The results obtained by changing the rations of phenol–benzophenone are summarized in Table I.

TABLE I

THE PHOTOCHEMICAL ACID-CATALYZED REACTION OF BENZOPHENONE WITH 2,6-DI-*t*-BUTYLPHENOL IN METHANOL

Run no.	2,6-Di-*t*-butylphenol, mmoles	Benzophenone, mmoles	Methanol, ml	Acid (ml)	Reacn time, hr	Yield of III, %
1	20	10	60	HCl (0.1)	24	46
2	20	15	60	H_2SO_4 (0.2)	21	59
3	20	20	60	H_2SO_4 (0.2)	24	66
4	20	30	60	HCl (0.1)	19	64
5	20	35	60	HCl (0.1)	24	68

Photochemical formation of III also proceeds in solvents other than methanol if a trace of mineral acid is present. The nature of the solvent, however, does affect the yield of III. In nonalcoholic solvents, brown by-products are formed upon irradiation, thereby impairing the absorbance of light by benzophenone. Alcohols which are more easily photooxidized by benzophenone than methanol lead to lower yields of bisphenol III. Table II lists the results obtained with different solvents.

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(15) E. A. Chandross and R. Kreilick, *J. Am. Chem. Soc.*, **85**, 2530 (1963).

(16) A. Rieker, H. Kaufmann, R. Mayer, and E. Müller, *Z. Naturforsch.*, **19b**, 558 (1964).

(17) E. A. Chandross and R. Kreilick, *J. Am. Chem. Soc.*, **86**, 117 (1964).

(18) W. T. Grubb and G. B. Kistiakowsky, *ibid.*, **72**, 419 (1940).

(19) Stimulating discussions on this subject with Dr. W. T. Grubb are gratefully acknowledged.

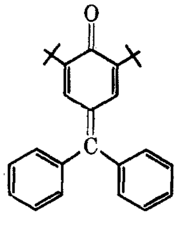
TABLE II

THE EFFECT OF SOLVENT ON THE YIELD OF III[a]

Solvent	Yield of III, %
CH_3OH	65
C_2H_5OH	43
$CH_3CHOHCH_3$	42
$(CH_3)_3COH$[b]	61
CH_3COCH_3	55
CH_3CN	51
CH_3COOH	42

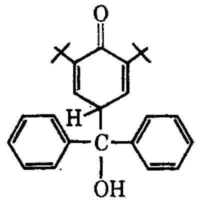
[a] Experimental conditions: 55 ml of solvent, 0.1 ml of concentrated HCl, 20 mmoles of 2,6-di-*t*-butylphenol, 35 mmoles of benzophenone; reaction time 21 hr; reaction temperature 16°; nitrogen atmosphere. [b] Reaction temperature 25°.

The presence of a trace of mineral acid is quite essential for a clean photochemical reaction and high yield. Irradiation in the absence of acid leads to 3,5-di-*t*-butylfuchsone (VII, 15%) when benzophenone and 2,6-di-*t*-butylphenol are used in a 1:1 ratio, while excess benzophenone leads to a mixture of bisphenol III (15%) and fuchsone VII (11%) in low yields.

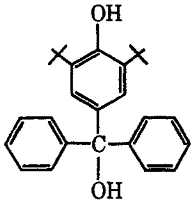


VII

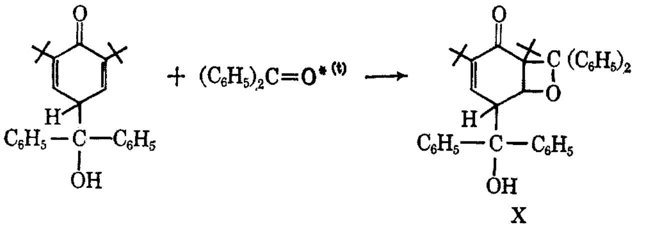
The formation of 3,5-di-*t*-butylfuchsone suggested that the photochemical reaction of benzophenone and 2,6-di-*t*-butylphenol involved the oxidation of 2,6-di-*t*-butylphenol by photoexcited benzophenone, and the coupling of the 2,6-di-*t*-butylphenoxy radical with the benzophenone ketyl radical thus formed to give 4-diphenylcarbinol-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (VIII). This assumption was verified by preparing the phenolic rearrangement product of VIII, 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (IX), by photochemical reaction of benzophenone with 2,6-di-*t*-butylphenol in acetone solution in the absence of acid. As a by-product in this reaction, the addition product of triplet-state benzophenone to the cyclohexadienone intermediate VIII was formed (X). This oxetane (X) was the only isolable product when benzene or acetic acid were chosen as solvent.



VIII



IX



X

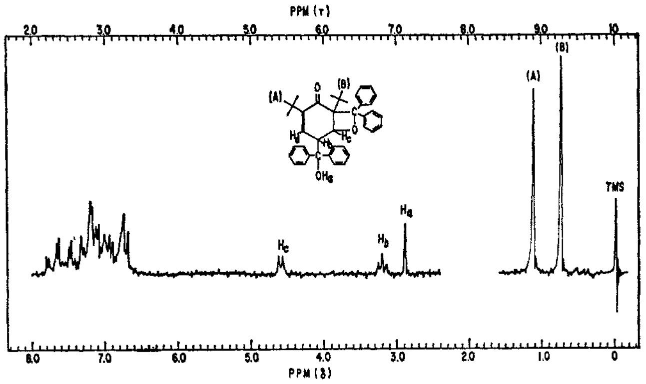
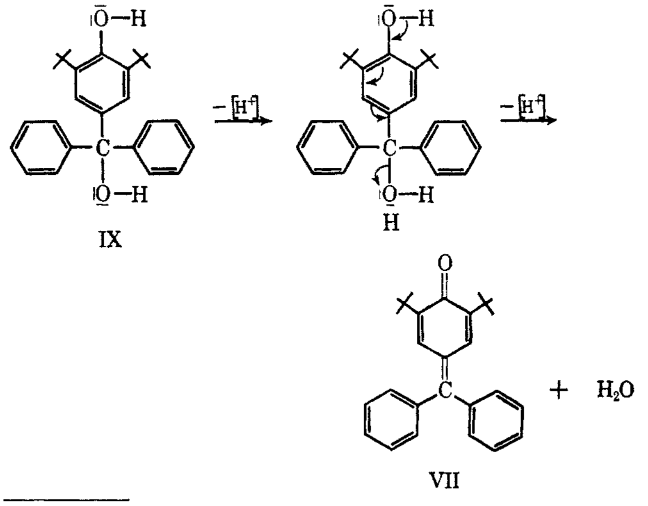


Figure 2.

The structure of X is supported by analytical and spectroscopic data. The structural assignment of X is based on the interpretation of its nmr spectrum (in deuteriochloroform; see Figure 2; the upfield region is run with smaller spectrum amplitude). The singlet was assigned H_a, since it was found to be exchangeable in D_2O. The doublet, caused by splitting by H_b represents H_c, while the triplet, caused by splitting by H_c and H_d represents H_b. The signal of H_d is hidden in the aromatic region. The geometrical assignment of the oxetane ring is based in the chemical shift of H_c and the shielding of one (upfield) *t*-butyl group by the phenyl rings.

The acid-catalyzed condensation of triphenylcarbinols with phenols to yield hydroxy-substituted tetraphenylmethanes is a well-known reaction (Baeyer–Villiger condensation) involving the intermediate formation of triphenylmethyl cations.[20–23] It thus appeared justified to assume an analogous reaction step in the photochemical formation of 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane when the formation of 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (IX) as a probable intermediate was demonstrated. Unexpectedly, however, it was not possible to bring about such an acid-catalyzed condensation between 2,6-di-*t*-butylphenol and the triphenylcarbinol IX. In the presence of catalytic amounts of mineral acid, IX was rapidly and quantitatively converted into 3,5-di-*t*-butylfuchsone (VII). In a convenient photochemical synthesis the fuchsone VII can be prepared



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[20] A. Baeyer and V. Villiger, *Ber.*, **35**, 3013 (1902).

[21] A. T. Shulgin, *J. Org. Chem.*, **27**, 3868 (1962).

[22] H. Schnell and H. Krimm, *Angew. Chem.*, **75**, 662 (1963).

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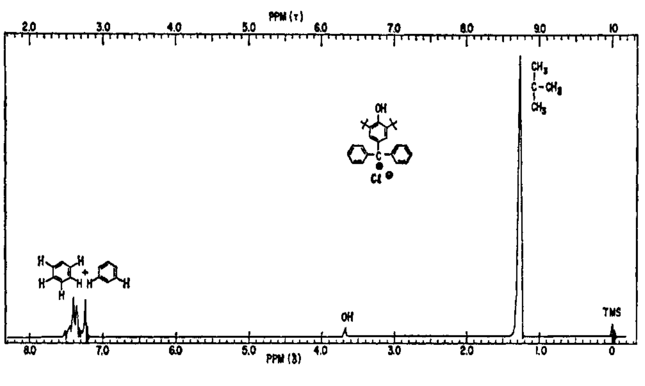


Figure 3.

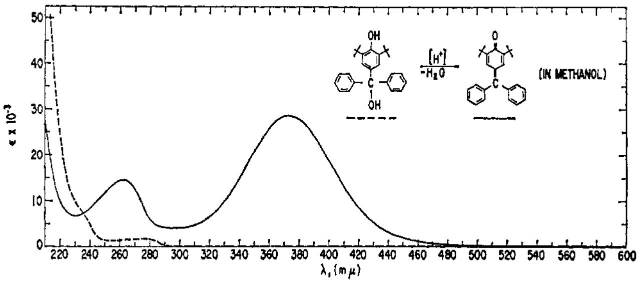
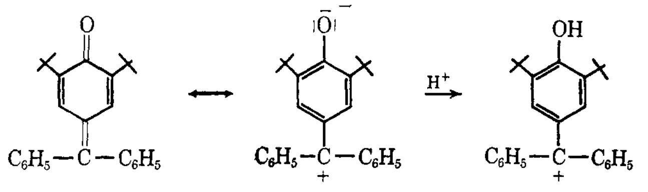


Figure 4.

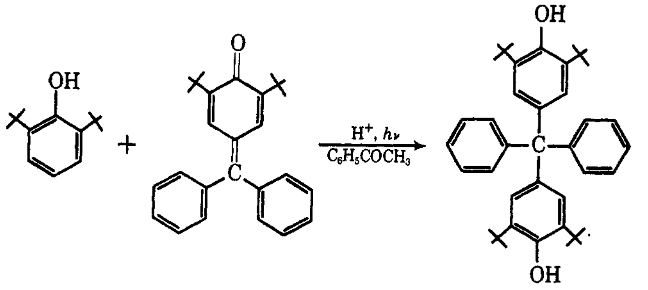
in an over-all yield of 47% by irradiating benzophenone (I) and 2,6-di-*t*-butylphenol (II) in acetone solution, followed by acidification of the reaction mixture without isolating the triphenylcarbinol IX.

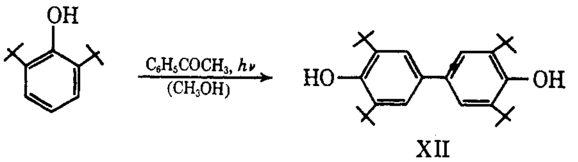
The mechanism of this acid-catalyzed reaction is readily understood and can be interpreted in terms of a protonation of the tertiary carbinol group and collapse of the carbonium ion formed by elimination of water.

Attempts were then made to bring about an acid-catalyzed reaction of 2,6-di-*t*-butylphenol with 3,5-di-*t*-butylfuchsone since protonation of fuchsone VII with strong acid to form the triphenylmethyl cation appeared feasible. Treatment of 3,5-di-*t*-butylfuchsone with HCl gas or concentrated sulfuric acid in methanol solution does lead to a deep red solution. However, no reaction with 2,6-di-*t*-butylphenol is observed. Dilution of the acidic solution leads to recovery of the fuchsone. Proton magnetic resonance investigation of the red species (prepared by treating VII with HCl gas in deuteriochloroform solution; see Figure 3) provided evidence for the quantitative formation of 3,5-di-*t*-butyl-4-hydroxytriphenylmethyl cation XI. Also, irradiation in the absence or presence of catalytical amounts of mineral acid seems to leave the strongly absorbing (see Figure 4) 3,5-di-*t*-butylfuchsone unattacked, even at a fuchsone concentration of 10^{-3} *M*. After addition of benzophenone, however, 2,6-di-*t*-butylphenol was found to react with 3,5-di-*t*-butylfuchsone upon irradiation to yield 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyltetraphenylmethane. More significantly, the photochemical addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone is also readily sensitized by acetophenone—a typical triplet sensitizer—(E_t = 76 kcal/mole), giving bisphenol III in over 90% yield. Irradiation of an acidified methanol solution of acetophenone and 2,6-di-*t*-butylphenol in the absence of 3,5-di-*t*-butylfuchsone results in the oxidation of 2,6-di-*t*-butylphenol to give 4,4'-dihydroxy-3,3'-5,5'-tetra-*t*-butylbiphenyl (XII). The acetophenone-sensitized addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone does proceed in the absence of the acid catalyst in methanol solution; the yield of III, however, is increased by addition of traces of mineral acid. Results obtained on the photosensitized addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone in methanol solution (given in Tables III and IV) clearly indicate that sensitization only occurs when the aromatic ketone is present in such quantities that it absorbs a considerable portion of the light. There appears to be no measurable formation of bisphenol III when about 99% of the light is absorbed by the fuchsone VII.[24]



VII VIIa XI





XII

Methanol appears to be a better solvent for the photosensitized addition reaction than acetone. Bisphenol III was found to be formed from 3,5-di-*t*-butylfuchsone and 2,6-di-*t*-butylphenol in acetone solution in a reaction sensitized by acetophenone, if hydrochloric acid was used as a catalyst, while sulfuric acid appeared to be ineffective. Sulfuric acid could be used in acetone solution, however, in the benzophenone sensitized addition reaction.

Naphthalene[25] was found to have an effect on all photochemical reactions described here. The yield of bisphenol III in the direct photochemical formation from benzophenone and 2,6-di-*t*-butylphenol in methanol solution decreased from 68 to 38%. The yield of 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (X, prepared in acetone solution) was decreased by the presence of naphthalene from 46 to 20%. Naphthalene was also found to impair effectively the photosensitized addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone (in methanol solution), decreasing the yield of the

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[24] This finding makes a mechanism involving two intermolecular energy transfers, as established for the benzophenone-sensitized dimerization of coumarine, improbable; *cf.* G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964).

[25] *Cf.* H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

TABLE III

THE SENSITIZED ADDITION OF 2,6-DI-*t*-BUTYLPHENOL (II) TO 3,5-DI-*t*-BUTYLFUCHSONE (VII)

Run no.	II, mmoles	VII, mmoles	Sensitizer (mmoles)	CH_3OH, ml	Acid (ml)	Time, hr	Yield of products, %: Recvd VII	III
1	0.5	0.5	...	500	HCl (0.2)	45	92	..
2	5	5	$(C_6H_5)_2CO$ (0.5)	60	HCl (0.1)	23	89	2
3[a]	2	1	$C_6H_5COCH_3$ (1.0)	150	HCl (0.2)	21	92	..
3[a]	2	1	$C_6H_5COCH_3$ (10)	150	HCl (0.2)	21	15	59
5[a]	2	1	$C_6H_5COCH_3$ (50)	150	HCl (0.2)	5	..	77
6	10	5	$C_6H_5COCH_3$ (100)	60	HCl (0.2)	18	..	94

[a] Experiments conducted at 20°.

TABLE IV

THE SENSITIZED ADDITION OF 2,6-DI-*t*-BUTYLPHENOL (II) TO 3,5-DI-*t*-BUTYLFUCHSONE (VII) IN METHANOL[a]

Run no.	II, mmoles	VII, mmoles	Sensitizer (mmoles)	Acid (ml)	Reacn time, hr	Naphthalene, g	Yield of products, %: Recvd VII	III
1	20	2.5	$(C_6H_5)_2CO$ (20)	H_2SO_4 (0.2)	17	...	..	59[b]
2	25	5	$(C_6H_5)_2CO$ (10)	HCl (0.1)	17	...	..	46[c]
3	4	2.5	$(C_6H_5)_2CO$ (10)	HCl (0.1)	24	1.0	65	5.5[d]
4	5	2.5	$C_6H_5COCH_3$ (33)	HCl (0.1)	14	...	..	79
5	5	2.5	$C_6H_5COCH_3$ (33)	...	14	...	..	50.6
6	5	2.5	$C_6H_5COCH_3$ (33)	HCl (0.1)	20	1.0	63	9

[a] Sixty milliliters of solvent. [b] Yield based on phenol plus fuchsone. [c] Yield based on benzophenone plus fuchsone. [d] Yield based on fuchsone.

bisphenol III by a factor of 10.[26] It has not been studied, however, to what extent the effect of naphthalene is due to photophysical quenching of triplet energy or is due to light filtering.

Discussion

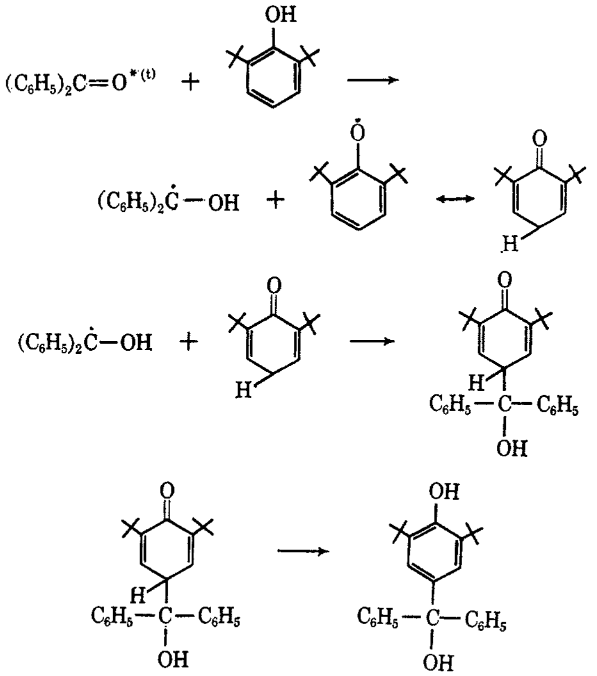
Based on the well-documented photophysical behavior of benzophenone the primary steps of the photochemical reaction reported here are to be described in terms of an n-π^* transition followed by intersystem crossing to give triplet-state benzophenone. The next

$$(C_6H_5)_2C{=}O + h\nu \longrightarrow (C_6H_5)_2C{=}O^{*(s)} \qquad (1)$$

$$(C_6H_5)_2C{=}O^{*(s)} \longrightarrow (C_6H_5)_2C{=}O^{*(t)} \qquad (2)$$

step conceivably involves the photochemical dehydrogenation of 2,6-di-*t*-butylphenol by triplet-state benzophenone leading to 2,6-di-*t*-butylphenoxy radical and benzophenone ketyl radical. This radical pair then undergoes a coupling reaction, possibly favored by the cage effect,[27,28] to give 4-diphenylcarbinol-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (VIII). Cyclohexadienone VIII then rearranges (probably spontaneously) to 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (IX) (see eq 3–5).

The presence of the intermediate cyclohexadienone VIII is firmly established since it has been trapped with triplet-state benzophenone to give the oxetane X under reaction conditions which lead to the phenolic triphenylcarbinol (IX). The yield of the oxetane X indeed increases at the expense of IX if excess benzophenone is employed in the reaction with 2,6-di-*t*-butylphenol in acetone solution. Rearrangement of the cyclohexadienone to the phenol certainly is more rapid in such acidic solvents as methanol than in acetone. It is thus conceivable that the oxetane X is not formed in an acidified reaction medium in which the over-all reaction leads to 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyltetraphenylmethane.



(3)

(4)

(5)

Thus far the reaction of benzophenone with 2,6-di-*t*-butylphenol is a photochemical one. At that point, however, the reaction sequence leading to bisphenol III involves a nonphotochemical step; acid-catalyzed reaction of 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol leads to 3,5-di-*t*-butylfuchsone. As pointed out above,

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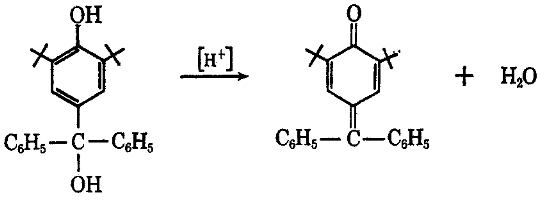
[26] The effect of naphthalene on this reaction step appears to be inconsistent with the effect of naphthalene on the over-all reaction and requires an explanation. It should be kept in mind that, under the experimental conditions necessarily applied for the photosensitized addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone (*i.e.*, irradiating a saturated solution of the fuchsone with most of the fuchsone suspended), the optical properties of the solution during this reaction step in the over-all reaction are not truly simulated, owing to the high extinction coefficient of the fuchsone. In the over-all reaction leading to the bisphenol III the fuchsone VII probably reacts further as it is formed.

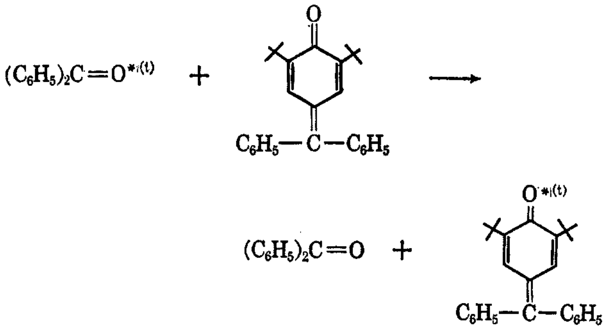
[27] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[28] Ultraviolet spectroscopic investigation of a solution of benzophenone (2×10^{-3} *M*) and 2,6-di-*t*-butylphenol (2×10^{-3} *M*) between 300 and 400 mμ did not reveal any association (complex formation) of the phenol with the ketone in the ground state.



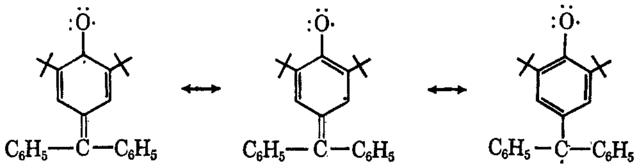
(6)

all nonphotochemical attempts to bring about an acid-catalyzed addition of 2,6-di-*t*-butylphenol to the fuchsone failed. Photochemical addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone was accomplished, however, by *sensitizing* the reaction with either benzophenone or acetophenone. This result apparently is best interpreted in terms of a triplet–triplet energy transfer from the sensitizer to 3,5-di-*t*-butylfuchsone.

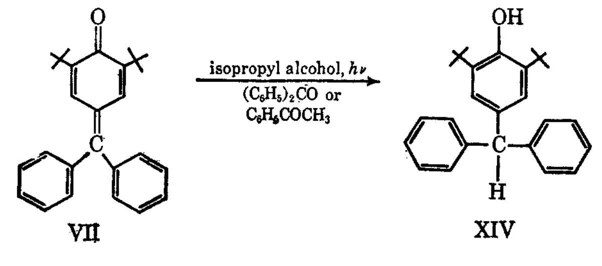

(7)

XIII

Three of the ten possible resonance contributors with biradical structure to the triplet-state 3,5-di-*t*-butylfuchsone (XIII) are shown here (XIIIa–XIIIc).


XIIIa XIIIb XIIIc

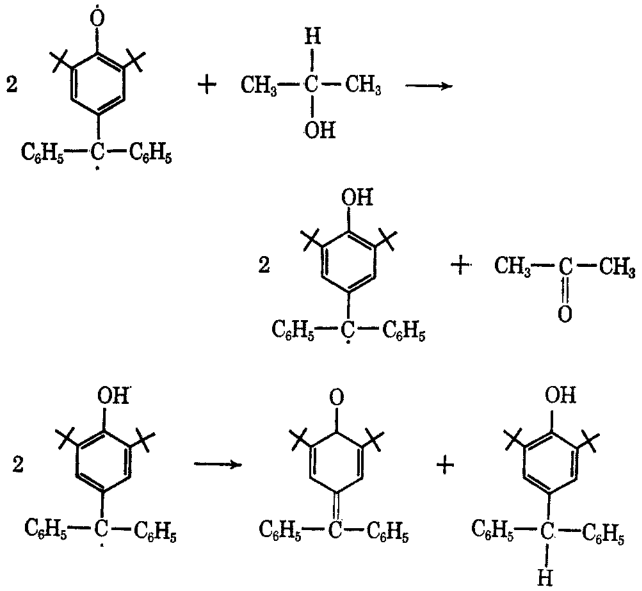
It follows from the triplet energy values[13] of the sensitizers employed in this work that the triplet energy of 3,5-di-*t*-butylfuchsone is probably lower than 69 kcal/mole (E_t of benzophenone). That the 3,5-di-*t*-butylfuchsone rather than the 2,6-di-*t*-butylphenol is the acceptor of triplet energy from the sensitizer is experimentally supported. Irradiation of benzophenone in isopropyl alcohol solution containing 2,6-di-*t*-butylphenol gives benzpinacol (79%) and acetone. Only a small amount of 2,6-di-*t*-butylphenol is consumed (analyzed by vapor phase chromatography) and this is accounted for by the formation of 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol (IX, 11%). There is no oxidation product of 2,6-di-*t*-butylphenol, *e.g.* XII, detectable. Irradiation of a solution of benzophenone in isopropyl alcohol in the presence of the *per se* photochemically stable 3,5-di-*t*-butylfuchsone (VII), however, does not result in the formation of benzpinacol but leads to 3,5-di-*t*-butyl-4-hydroxytriphenylmethane (XIV) in over 90% (isolated) yield. Formation of benzpinacol is first observed when the conversion of VII into XIV is completed. Thus, benzophenone is a sensitizer for the photochemical reduction of 3,5-di-*t*-butylfuchsone. Acetophenone was found to react in the same manner.



VII XIV

This reaction apparently demonstrates the biradical character of triplet-state 3,5-di-*t*-butylfuchsone. In the absence of mineral acid and nucleophilic 2,6-di-*t*-butylphenol it reacts by abstracting hydrogen atoms from the solvent. The mechanism of this photosensitized reduction could proceed according to Scheme II.[29]

Dimerization of the intermediate triphenylmethyl radical—a reaction formally analogous to the photo-



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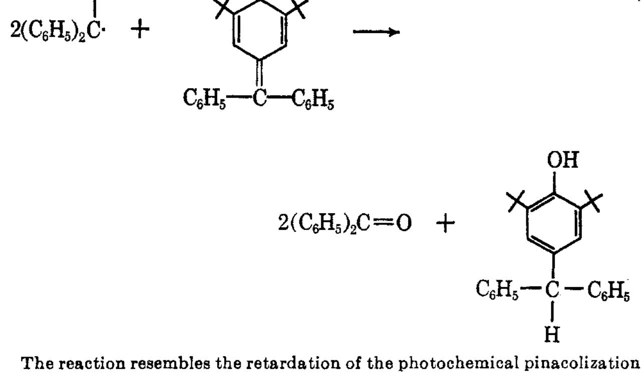
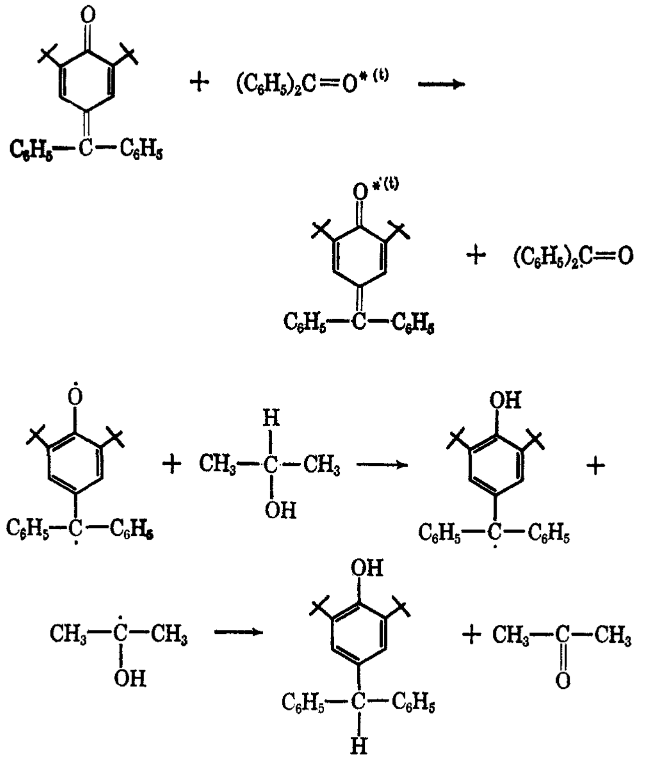
(29) Benzophenone and acetophenone are the only sensitizers used and found effective for the photoreduction of VII. Both ketones are known to abstract hydrogen atoms from isopropyl alcohol to give ketyl radicals. One possible mechanism for the reduction of VII, besides the one based on triplet-triplet energy transfer (a), could involve a hydrogen atom transfer *via* ketyl radicals, formally according to the following.



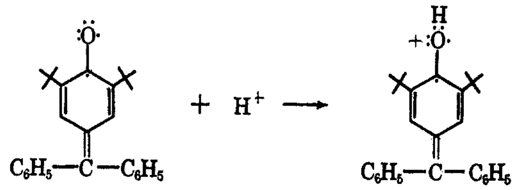
The reaction resembles the retardation of the photochemical pinacolization of benzophenone by mercaptans, as studied by S. G. Cohen, S. Orman, and D. A. Laufer, *J. Am. Chem. Soc.*, **84**, 3905 (1962); see also ref 10.

SCHEME II



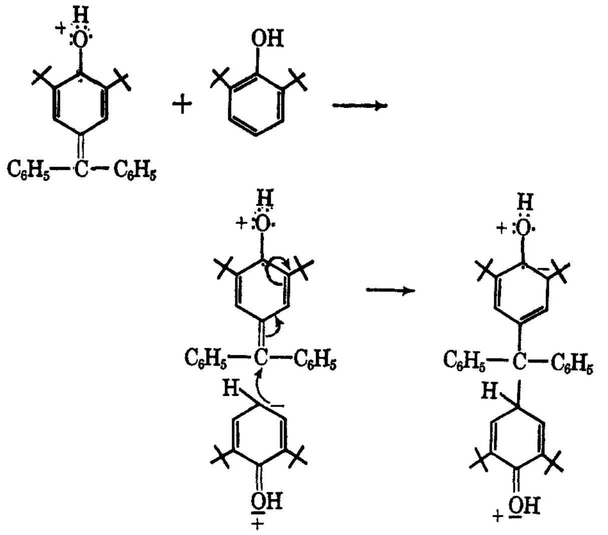
chemical formation of benzpinacol from benzophenone—cannot be expected because of steric hindrance. It is quite possible, however, that the intermediate triphenylmethyl radical leads to the triphenylmethane XIV *via* a disproportionation reaction rather than by direct hydrogen abstraction from the solvent.

Based on the observation that the photosensitized addition of 2,6-di-*t*-butylphenol to the fuchsone is acid catalyzed, reaction step 8, involving protonation of triplet-state 3,5-di-*t*-butylfuchsone, depicted here with one resonance contributor, results in the formation of a triplet-state cation (XV).



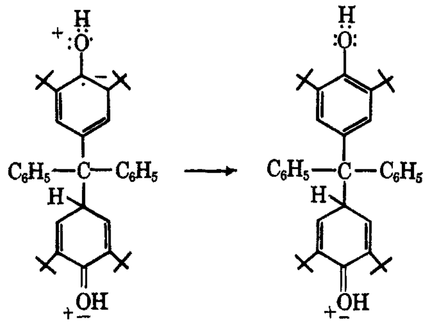
XV (8)

The description of the photosensitized excitation of 3,5-di-*t*-butylfuchsone in terms of the formation of a "polar state"[30] intermediate (depicted in structure VIIa) appears to be quite inadequate in view of the experimental evidence presented above indicating that the 3,5-di-*t*-butyl-4-hydroxytriphenylmethyl cation (XI) does not react with 2,6-di-*t*-butylphenol. The photosensitized addition of 2,6-di-*t*-butylphenol to 3,5-di-*t*-butylfuchsone, therefore, is best described as the reaction of the *triplet-state* triphenylmethyl cation (XV) as depicted in reaction 9.

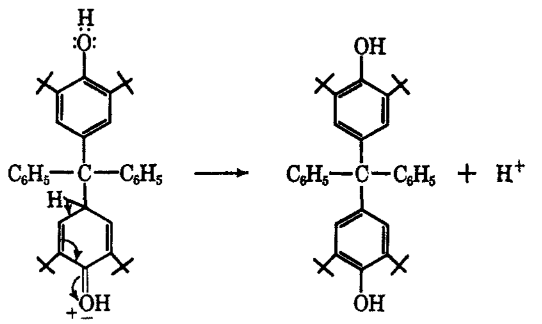


(9)

The final two reaction steps involving an electronic transition (10) ("electron demotion"[31]) and loss of proton (11) lead to 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane.



(10)



(11)

The fact that bisphenol III cannot be prepared by direct irradiation of a solution of fuchsone VII and 2,6-di-*t*-butylphenol can probably be explained by self-quenching of fuchsone singlets ($F^{*(s)}$). This is supported by the finding that irradiation of 3,5-di-*t*-butylfuchsone and 2,6-di-*t*-butylphenol at a concentration of 5 × 10^{-5} *M* in acidified methanol solution results in a very slow reaction. However, even after 21 hr of irradiation, vapor phase chromatographic analysis still shows unreacted fuchsone VII and phenol II as well as four peaks, three of which have retention times corresponding to bisphenol III, benzophenone (major product), and 2,6-di-*t*-butyl-1,4-benzoquinone, respectively. Likewise, irradiation of a 5 × 10^{-5} *M* solution of fuchsone VII in isopropyl alcohol was found to result in a reaction. Vapor phase chromatographic analysis of the reaction mixture indicates the formation of 3,5-di-*t*-butyl-4-hydroxytriphenylmethane (XIV, major product), benzophenone (minor product), and 3,5-di-*t*-butyl-1,4-benzoquinone (minor product), as well as the unidentified compound (major product) observed

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(30) *Cf.* O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(31) *Cf.* H. E. Zimmerman, *ibid.*, **1**, 183 (1963).

in the irradiation experiment in methanol solution. These findings suggest that direct photochemical excitation of 3,5-di-*t*-butylfuchsone gives singlet fuchsone leading to several products if self-quenching is made improbable owing to high dilution. The formation of the triplet-state products III and XIV in experiments conducted at low concentrations in the absence of a sensitizer indicates that intersystem crossing

$$F^{*(s)} \longrightarrow F^{*(t)}$$

can occur as well as chemical reaction of $F^{*(s)}$.

The uniqueness of the intriguingly simple looking over-all reaction

$$\mathrm{I} + \mathrm{II} \xrightarrow[\text{[H}^+\text{]}]{h\nu} \mathrm{III} + H_2O$$

lies in the fact that all reaction participants are involved in more than just one mode of reaction. Photoexcited benzophenone displays its properties as an oxidizing agent, and it participates in a photophysical triplet energy transfer reaction. 2,6-Di-*t*-butylphenol is oxidized to give a phenoxy radical, and it is also involved in a quasi-ionic condensation reaction. The protons, finally, are essential for the ground-state formation of the photophysically active key intermediate, 3,5-di-*t*-butylfuchsone, and for the formation of an excited-state cation derived from this intermediate.

Experimental Section

The Apparatus.—All irradiations were carried out by using an internally water-cooled illuminating annular space reactor (i.d. 50 mm) made of Pyrex glass, assembled by means of standard-tapered fittings and equipped with gas fittings for inert gas blanketing. The illuminated reaction zone had a thickness of 5 mm. The lamp used was a G.E. 100-w mercury lamp, Type H-100 A4/T, from which the glass jacket was removed. All irradiations were carried out at 14–16° *under nitrogen* passed through a frit into the reaction mixture. For irradiation requiring elevated temperature, as in the case when *t*-butyl alcohol was used as solvent, a thermostat was employed.

Materials.—Absolute methanol was commercial grade. 2,6-Di-*t*-butylphenol was vacuum distilled before use, giving a colorless material. Benzophenone, mp 48–49°, was commercial grade and used without further purification. All melting points were taken on a Fisher-Johns melting point apparatus and are not corrected.

4,4′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (III).—A solution of 2,6-di-*t*-butylphenol (4.12 g, 20 mmoles) and benzophenone (1.0 g) in 55 ml of absolute methanol containing 0.1 ml of concentrated hydrochloric acid was irradiated for 24 hr. During the course of the reaction additional benzophenone was added after 1 hr (1.0 g), 2 (1.0 g), 5 (1.0 g), 6 (1.46 g), and 21 hr (0.91 g). (The total amount of benzophenone added was 35 mmoles. Precipitation of colorless crystals began about 45 min after starting irradiating.) The light yellow reaction mixture was diluted with 100 ml of methanol and boiled for 3 min in order to dissolve co-precipitated benzpinacol. Filtration yielded 3.75 g of colorless crystals, mp 235°. Recrystallization from hot chloroform by addition of methanol did not raise the melting point.

Anal. Calcd for $C_{41}H_{52}O_2$ (576.87): C, 85.37; H, 9.09. Found: C, 85.25; H, 9.10; mol wt, 563 (thermoelectric measurement in chloroform).

From the filtrate an additional 0.17 g of III was isolated by filtration after 24 hr. The total yield of III was 3.92 g (68%). If the total amount of benzophenone is added in one portion at the beginning of the irradiation, the yield drops only slightly to 65%.

Evaporation of the filtrate of the reaction mixture and treatment of the residue with petroleum ether gave 2.5 g of benzpinacol. Upon evaporation, the filtrate gave a brown, oily residue from which no identifiable product could be isolated.

The results obtained on other photochemical reactions of benzophenone with 2,6-di-*t*-butylphenol in methanol solution are summarized in Table V.

TABLE V

THE REACTION OF BENZOPHENONE (I) WITH 2,6-DI-*t*-BUTYLPHENOL (II) IN METHANOL[a]

Run no.	I, mmoles	II, mmoles	Acid (ml)	Naphthalene, g	Yield of products, % IX	VII	III
1	35	20	HCl (0.1)	1.0	. . .	. .	38
2	10	10	. . .	. . .	4[b]	15	. . .
3	10	10	. . .	1.0	9.5[b]	. .	. . .
4	20	10	. . .	. . .	. . .	11	15.5

[a] Sixty milliliters of solvent; reaction time 24 hr. [b] Isolated VII after acidification.

Oxidation of 4,4′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane.—A suspension of active manganese dioxide (10 g) in a solution of III (2 g) in benzene (200 ml) placed in a screw-cap bottle under nitrogen was shaken for 20 min. The active manganese dioxide was then removed by filtration and washed with benzene. Evaporation of the combined orange filtrates yielded 2 g of orange bispirodienone IV (100%), mp 256–258° dec. The substance can easily be recrystallized by dissolving in warm chloroform and addition of methanol. The melting point, depending on the rate of heating, can range from 253–254° (slow heating) to 263–264° (substance put on hot stage at 240°). The compound exhibits thermochromism in the solid state and in solution, turning deep ruby red upon heating.

Anal. Calcd for $C_{41}H_{50}O_2$ (574.86): C, 85.67; H, 8.77. Found: C, 85.62; H, 8.64; mol wt, 550 (thermoelectric measurement in benzene).

Reduction of IV.—Concentrated hydrochloric acid (1 ml) was added to a suspension of zinc dust (1 g) in a solution of the bispirodienone IV compound (288 mg, 0.5 mmole) in 30 ml of chloroform. Upon stirring for 1 min, the solution was completely colorless. Filtration and evaporation of the filtrate yielded 280 mg of 4,4-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane, mp 234–235°. Mixture melting point with authentic sample showed no depression (yield 97%).

3,5-Di-*t*-butylfuchsone (VII). A. From the Photochemical Reaction of Benzophenone with 2,6-Di-*t*-butylphenol in Acetone Solution.—A solution of benzophenone (1.82 g, 10 mmoles) and 2,6-di-*t*-butylphenol (4.12 g, 20 mmoles) in acetone (75 ml) was irradiated for 14 hr. The very light yellow solution was then evaporated *in vacuo* at room temperature and the light yellow, oily residue was dissolved in 70 ml of methanol. Addition of 10 drops of concentrated sulfuric acid in 1 ml of methanol led to precipitation of yellow, needle-shaped crystals (yield 1.75 g, 47%), mp 182°. Recrystallization by dissolving in a little petroleum ether (bp 30–60°) or chloroform and addition of methanol raised the melting point to 183–184° (lit.[32] 177–178°).

Anal. Calcd for $C_{27}H_{30}O$ (370.54): C, 87.52; H, 8.16. Found: C, 87.50; H, 7.89; mol wt, 366 (thermoelectric measurement in benzene).

From the above methanol filtrate 150 mg (5.3%) of oxetane X crystallized after 3 hr of standing.

The same yields of VII and X were obtained when a solution of 10 mmoles of benzophenone and 15 mmoles of 2,6-di-*t*-butylphenol in 75 ml of acetone was irradiated for 10 hr.

Irradiating a solution of 10 mmoles of 2,6-di-*t*-butylphenol and 15 mmoles of benzophenone in 75 ml of acetone for 10 hr leads to a decreased yield of 3,5-di-*t*-butylfuchsone (32%, after acidification) and an increased yield of oxetane X (14%). The reaction mixture was in that case best worked up by evaporating the acetone solution and dissolving the oily residue in methanol (50 ml), whereupon the oxetane precipitated. The fuchsone was then precipitated by adding a trace of mineral acid to the methanol filtrate.

B. From 3,5-Di-*t*-butyl-4-hydroxytriphenylcarbinol.—3,5-Di-*t*-butyl-4-hydroxytriphenylcarbinol (388 mg, 1 mmole) was dissolved in methanol (10 ml). Addition of 1 drop of concentrated hydrochloric acid in 1 ml of methanol causes immediate precipitation of 3,5-di-*t*-butylfuchsone (yield 360 mg, 97%), mp 183°.

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(32) E. Müller, R. Mayer, U. Hellmann, and K. Scheffler, *Ann.*, **645**, 66 (1961).

TABLE VI

THE PHOTOCHEMICAL REACTIONS OF 2,6-DI-*t*-BUTYLPHENOL (II) AND 3,5-DI-*t*-BUTYLFUCHSONE (VII) IN ACETONE SOLUTION[a]

Run no.	II, mmoles	VII, mmoles	Sensitizer, (mmoles)	Acid (ml)	Reacn time, hr	Naphthalene, g	Yield of products, %		
							IX	Recvd VII	III
1	15	...	$(C_6H_5)_2CO$ (10)	...	10	...	46[b]	...	...
2	15	...	$(C_6H_5)_2CO$ (10)	...	10	1.0	20[b]	...	...
3	20	...	$(C_6H_5)_2CO$ (20)	HCl (0.5)	22	...	..	...	51
4	5	2.5	$(C_6H_5)_2CO$ (2)	H_2SO_4 (0.2)	15	...	..	59.5	27.8[c]
5	5	2.5	$C_6H_5COCH_3$ (33)	...	16	...	..	81	...
6	5	2.5	$C_6H_5COCH_3$ (33)	H_2SO_4 (0.2)	13	...	..	98	...
7	5	2.5	$C_6H_5COCH_3$ (33)	HCl (0.3)	19	...	..	*d*	20.8

[a] Seventy-five milliliters of solvent. [b] Isolated as fuchsone after acidification. [c] Yield based on fuchsone VII plus phenol II. [d] Yield of recovered fuchsone VII accidentally not determined.

Photosensitized addition reactions to 3,5-di-*t*-butylfuchsone are summarized in Table III (see also Table IV). The experimental procedure involved irradiation of a solution in which part of the 3,5-di-*t*-butylfuchsone remained suspended. The fuchsone VII dissolved during the course of the irradiation while the bisphenol III precipitated. In some experiments excess sensitizer was removed from the irradiated reaction mixture by vacuum distillation. Bisphenol III was easily isolated owing to its very low solubility in methanol.

3,5-Di-*t*-butyl-4-hydroxytriphenylcarbinol (IX).—A solution of benzophenone (18.2 g, 100 mmoles) and 2,6-di-*t*-butylphenol (20.6 g, 100 mmoles) in 150 ml of acetone was irradiated for 19 hr. The solvent was then evaporated at room temperature *in vacuo* and the light yellow, oily residue was subjected to molecular distillation. After the unreacted starting materials the 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol was distilled at a bath temperature of 180–185°, forming a light yellow glass at room temperature. Upon treatment with petroleum ether (bp 30–60°) the substance formed colorless crystals. It was recrystallized from hot petroleum ether, mp 151–152°.

Anal. Calcd for $C_{27}H_{32}O_2$ (388.56): C, 83.46; H, 8.30. Found: C, 83.39; H, 8.24; mol wt, 373 (thermoelectric measurement in benzene).

The yield of IX was 6 g (15.5%). The distillation, however, had not been carried out to completion since prolonged heating of the residue resulted in the formation of 3,5-di-*t*-butylfuchsone.

In a comparison experiment the oily residue obtained after evaporation of the acetone *in vacuo* was dissolved in 100 ml of methanol and acidified with 1 drop of concentrated hydrochloric acid dissolved in 1 ml of methanol to yield 12 g of fuchsone VII (32%).

Photochemical reactions in acetone solution are summarized in Table VI.

Oxetane X.—A solution of 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles) and benzophenone (4.55 g, 25 mmoles) in 50 ml of benzene was irradiated for 26 hr. The light yellow reaction mixture was then evaporated *in vacuo* and the sticky residue was dissolved in 50 ml of methanol. After a few hours, colorless crystals started precipitating. After 24 hr the precipitate was removed by filtration, washed with methanol, and recrystallized from hot benzene by addition of methanol. The yield was 0.76 g (13%), mp 272°.

Anal. Calcd for $C_{40}H_{42}O_3$ (570.78): C, 84.17; H, 7.42. Found: C, 84.19; H, 7.68; mol wt, 568 (thermoelectric measurement in chloroform).

The filtrate was evaporated and the oily residue was treated with petroleum ether (bp 30-60°) to yield 0.7 g of benzpinacol.

For a preparation of oxetane X from benzophenone and 2,6-di-*t*-butylphenol in acetone solution, see the preparation of 3,5-di-*t*-butylfuchsone (VII).

Photochemical Reaction of Acetophenone with 2,6-Di-*t*-butylphenol (XII).—A solution of 2,6-di-*t*-butylphenol (4.12 g, 20 mmoles) and acetophenone (3 g, 25 mmoles) in 60 ml of methanol containing 0.1 ml of concentrated hydrochloric acid was irradiated under nitrogen for 22 hr. The yellow solution was evaporated at room temperature, leaving a dark brown residue from which 850 mg (20%) of 4,4′-dihydroxy-3,3,5′-tetra-*t*-butyldiphenyl (XII) was removed by filtration, mp 186–188°. Mixture melting point with authentic material showed no depression.

Irradiation of Benzophenone in Isopropyl Alcohol in the Presence of 2,6-Di-*t*-butylphenol.—A solution of benzophenone (3.64 g, 20 mmoles) and 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles) in 60 ml of isopropyl alcohol was irradiated for 5 hr. Precipitation of benzpinacol started 1 hr after the beginning of the irradiation. The colorless reaction mixture was evaporated and the solid residue was triturated in 40 ml of methanol and filtered, giving 2.3 g of benzpinacol, mp 185–188°. The methanol filtrate containing 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol was acidified with 1 drop of concentrated hydrochloric acid to give 0.4 g (11%) of 3,5-di-*t*-butylfuchsone, mp 182°, as precipitate. The filtrate was evaporated and the residue was treated with 50 ml of petroleum ether (bp 30–60°), leaving an additional 0.6 g of benzpinacol undissolved. Total yield of benzpinacol was 2.9 g (79%).

3,5-Di-*t*-butyl-4-hydroxytriphenylmethane (XIV). A. Reduction of 3,5-Di-*t*-butylfuchsone with Zinc–Hydrochloric Acid.—Concentrated hydrochloric acid (20 ml) was added to a stirred suspension of zinc powder (10 g) and 3,5-di-*t*-butylfuchsone (1.110 g, 3 mmoles) in 100 ml of methanol. The mixture was refluxed for 10 min, then filtered hot through a sintered-glass funnel, and the residual zinc powder was washed with little warm methanol. The filtrate was slowly diluted with 30 ml of water and the colorless, crystalline precipitate was recrystallized from hot methanol containing few drops of concentrated hydrochloric acid, giving needle-shaped, colorless crystals, mp 135–136° (lit.[32] 133–134°) (yield 1.0 g, 90%).

Anal. Calcd for $C_{27}H_{32}O$ (372.56): C, 87.05; H, 8.66. Found: C, 87.10; H, 8.70; mol wt, 366 (thermoelectric measurement in benzene).

B. Reduction of 3,5-Di-*t*-butylfuchsone with Sodium Borohydride.—Sodium borohydride (3.7 g, 100 mmoles) was added to a suspension of 3,5-di-*t*-butylfuchsone (1.110 g, 3 mmoles) in methanol, resulting in an exothermic reaction. After 5 min the reaction mixture was filtered. Dilution of the filtrate with water gave 1.10 g (99%) of 3,5-di-*t*-butyl-4-hydroxytriphenylmethane, mp 134–136°.

C. Benzophenone-Sensitized Reduction of 3,5-Di-*t*-butylfuchsone in Isopropyl Alcohol.—3,5-Di-*t*-butylfuchsone (1.85 g, 5 mmoles) was suspended in isopropyl alcohol (100 ml) containing 18.2 g (100 mmoles) of benzophenone, and irradiated at 16°. After 3 hr of irradiation the fuchsone was completely dissolved, and after 8 hr of irradiation the solution was almost completely colorless when benzpinacol started precipitating. The irradiation was stopped 5 min later. Filtration gave 2 g of benzpinacol. The filtrate was evaporated *in vacuo*, the residue was subjected to distillation at about 1 mm and a bath temperature of 125–135°, thus removing the benzophenone (13 g). The residue was subjected to vacuum sublimation at about 1 mm and a bath temperature of 125–135°. The colorless sublimate was recrystallized from boiling methanol, giving 1.72 g (92%) of 3,5-di-*t*-butyl-4-hydroxytriphenylmethane, mp 135–136°. Mixture melting point with authentic material showed no depression.

D. Acetophenone-Sensitized Reduction of 3,5-Di-*t*-butylfuchsone.—A solution of 3,5-di-*t*-butylfuchsone (370 mg, 1 mmole) and acetophenone (12 g, 100 mmoles) in 180 ml of isopropyl alcohol was irradiated at 16°. When the solution turned colorless after 1.5 hr of irradiation, 370 mg of 3,5-di-*t*-butylfuchsone was added. During the course of the 10 hr of irradiation, 370 mg of the fuchsone were added after 3.5 and 6 hr. The solvent and the acetophenone were then removed from the light yellow solution by vacuum distillation. The oily residue crystallized upon treatment with petroleum ether and was recrystallized from boiling methanol (yield 1.2 g, 81%), mp 134–136°. Mixture melting point with authentic material obtained under A showed no depression.

Irradiation of 3,5-Di-*t*-butylfuchsone at Low Concentration. A. In the Presence of 2,6-Di-*t*-butylphenol.—A methanol solution (400 ml) containing 3,5-di-*t*-butylfuchsone (5.4 mg, 0.02 mmole), 2,6-di-*t*-butylphenol (4.12 mg, 0.02 mmole), and concentrated hydrochloric acid (0.8 ml) was irradiated for 21 hr. The yellow solution was then evaporated to dryness and the residue was dissolved in a few drops of methanol. A sample of this solution was subjected to vapor phase chromatography, using a 2-ft silicon gum column employing temperature programming (7.5°/min) between 100 and 280°. The retention times of the peaks observed were 7.8 (shoulder, 2,6-di-*t*-butylphenol), 8 (2,6-di-*t*-butylbenzoquinone), 10.8 (benzophenone), 22.8 (3.5-di-*t*-butylfuchsone), 23.8 (unknown photoproduct), and 31 min (bisphenol III).

B. In Isopropyl Alcohol.—A solution of 3,5-di-*t*-butylfuchsone (3.7 mg, 0.01 mmole) in isopropyl alcohol (200 ml) was irradiated. After 20 min, when the solution had become colorless, an additional 3.7 mg of VII was added. This addition of 3.7-mg portions was continued at 20-min intervals (whenever the solution turned colorless) until a total of 37 mg of VII had been added. The reaction mixture was then evaporated to dryness and the light yellow, sticky residue was dissolved in 1 ml of methanol. A sample of this solution was subjected to vapor phase chromatography as described under A. The retention time of the peaks observed were 7.8 (trace), 10.6 (trace), 21.5 (3.5-di-*t*-butyl-4-hydroxytriphenylmethane), and 23.5 min (unknown photoproduct). From the methanol solution 15 mg of XIV (26%) precipitated as colorless crystals during the next day. The compound was identified by its melting point (134°) and mixture melting point with authentic material.

Spectra.—The infrared spectra were taken on a Perkin-Elmer grating infrared spectrophotometer, Model 521. Ultraviolet spectra were obtained with a Cary recording spectrophotometer, Model 14. Proton magnetic resonance spectra were taken on a Varian A-60 spectrometer (using deuteriochloroform as solvent with tetramethylsilane as an internal standard). Electron spin resonance spectra were measured with a 3-cm epr spectrometer employing 100-kc modulation and a variable-temperature cavity.

Registry No.—I, 119-61-9; II, 128-39-2; III, 13135-05-2; IV, 13145-52-3; VII, 13131-76-5; IX, 13145-53-4; X, 13131-77-6; XII, 128-38-1; XIV, 13145-54-5.

Photochemical Reactions with Phenols. II. The Photochemical Reactions of Diaryl Ketones with Phenols[1]

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Received January 4, 1967

The photochemical reaction of substituted benzophenones with 2,6-disubstituted phenols has been investigated. Depending on the solvent and on the substituents of the phenols, the reaction can be terminated at various stages of a multistep reaction sequence. In acetone solution, diarylketones react with 2,6-disubstituted phenols to give 3,5-disubstituted 4-hydroxytriphenylcarbinols, which, in an acid-catalyzed reaction, can easily be converted into 3,5-disubstituted fuchsones. In acidified methanol, a variety of substituted benzophenones reacts with 2,6-di-*t*-butylphenol to give substituted tetraphenylmethanes in a unique, one-step procedure.

Chemical reactions of triplet-state ketones have been the subject of numerous photochemical studies.[2] Particularly, the effect of substituents on the pinacolization of benzophenone has been investigated recently.[3-5] Suitable hydrogen donors for the pinacolization are known to be solvents like alcohols,[6,7] hydrocarbons,[8] ethers,[9] or amines.[10]

Several years ago Bäckström and Sandros[11] in a study on the photochemistry of biacetyl had found that phenol is a much stronger quencher of the long-lived fluorescence of biacetyl than methanol or isopropyl alcohol. As a practical consequence of this observation, it appeared conceivable to us to dehydrogenate phenols by triplet-state ketones in methanol solution. In the preceding paper the photochemical reaction of benzophenone (I) with 2,6-di-*t*-butylphenol (II) in (acidified) methanol solution was shown to result in the oxidation of the phenol by triplet-state benzophenone. However, no pinacolization occurred, but coupling of the ketyl radical with the phenoxy radical, followed by a tautomerization, gave 4-hydroxy-3,5-di-*t*-butyltriphenylcarbinol (III). In a nonphotochemical reaction III was then converted into 3,5-di-*t*-butylfuchsone (IV), which, photosensitized by benzophenone, reacted with 2,6-di-*t*-butylphenol to yield 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (V) (Scheme I).

Because of its synthetic usefulness and in view of the uniqueness of the reaction sequence, it appeared interesting to investigate the photochemical reaction of substituted benzophenones with 2,6-disubstituted phenols.

Results

A. Photochemical Reaction of Substituted Benzophenones with 2,6-Disubstituted Phenols in Acetone Solution. 2,6-Di-*t*-butylphenol.—Irradiation of an acetone solution of benzophenone (Ia) and 2,6-di-*t*-butylphenol, employing light from a mercury arc filtered through Pyrex, results in the formation of 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol, which, in the presence of a trace of mineral acid, eliminates water to yield 3,5-di-*t*-butylfuchsone (IVa). In a similar manner, substituted benzophenones Ib–i react with 2,6-di-*t*-butylphenol to give fuchsones IVb–i, in an essentially one-step synthesis.

Table I lists the diaryl ketones employed and the reaction products obtained. The yields of isolated products are based on starting materials, but not on conversion. All fuchsones prepared in the course

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[1] For paper I, see the preceding paper: *J. Org. Chem.*, **32**, 2115 (1967).

[2] For a review article with pertinent references on the photochemical reactions of ketones in solution, see G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

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