trated 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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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).

(3) J. N. Pitts, Jr., H. W. Johnson, Jr., and I. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(4) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963); G. Porter and P. Suppan, *Pure Appl. Chem.*, **9**, 499 (1964).

(5) S. G. Cohen and M. N. Siddigui, *J. Am. Chem. Soc.*, **86**, 5047 (1964).

(6) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900).

(7) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963), and references cited therein.

(8) C. Walling and M. J. Givian, *J. Am. Chem. Soc.*, **87**, 3361 (1965), and references cited therein.

(9) S. G. Cohen and S. Aktipis, *Tetrahedron Letters*, 579 (1965).

(10) S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965).

(11) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

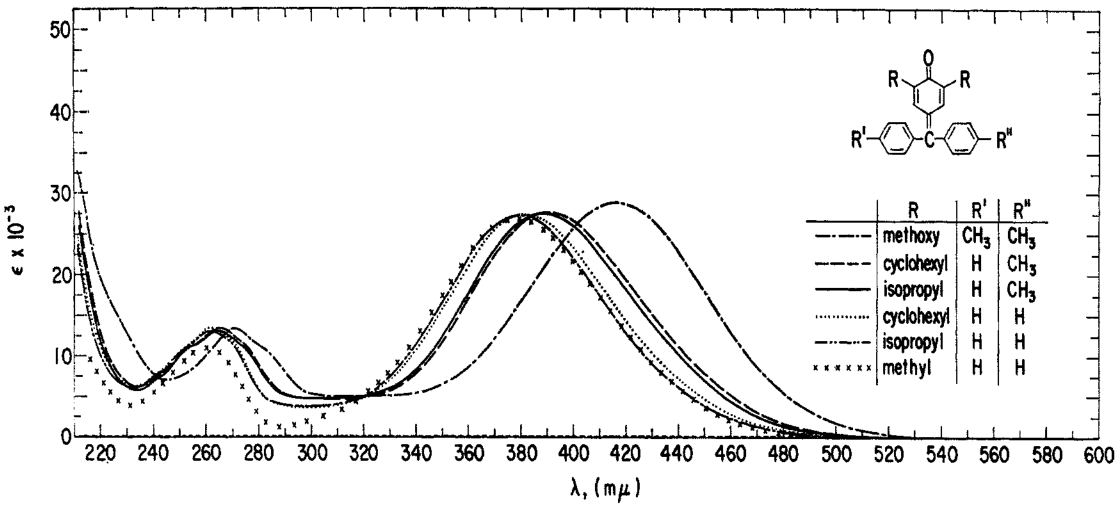


Figure 1.

Scheme I

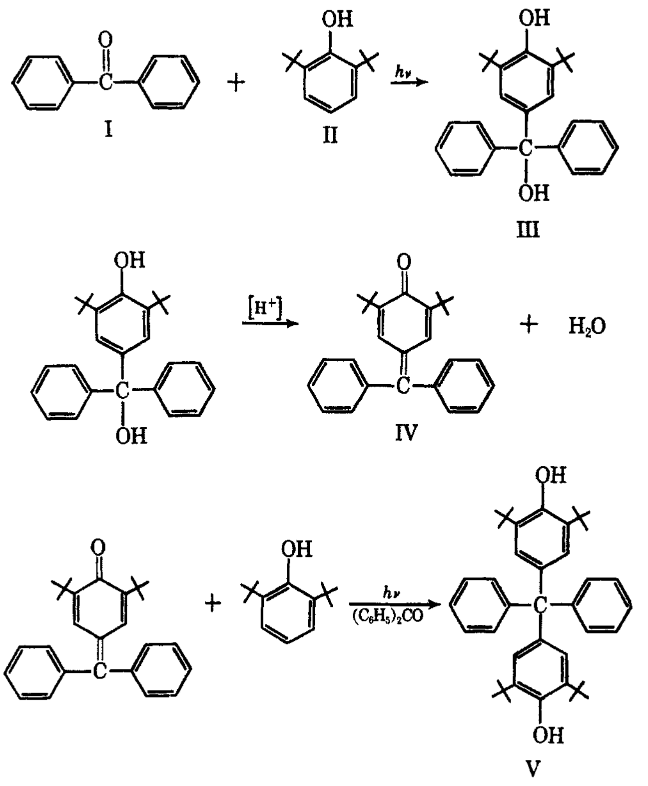
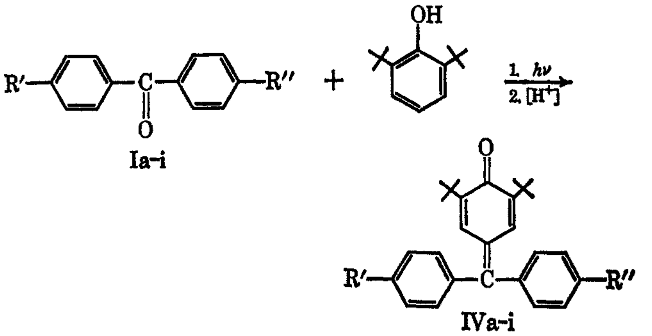


Table I



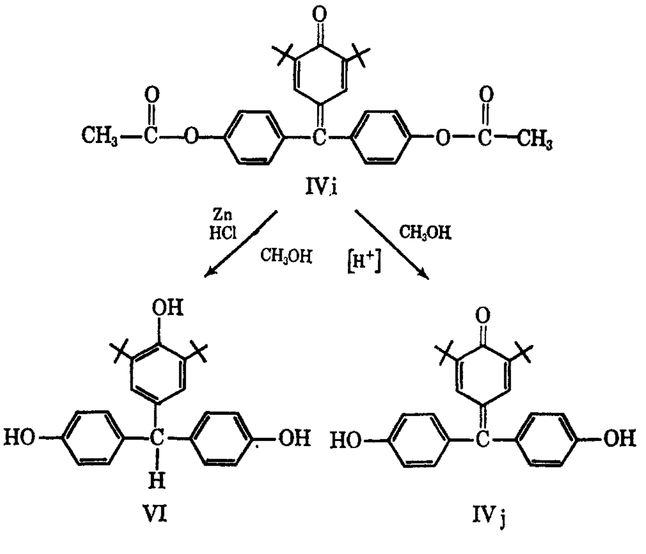
I and IV	R′	R″	Yield of IV, %
a	H	H	47
b	H	CH_3	57
c	H	Cl	52
d	H	Br	65
e	H	OH	51
f	H	$COOCH_3$	54
g	CH_3	CH_3	41
h	Cl	Cl	50
i	CH_3COO	CH_3COO	63

of this study represent stable, crystalline compounds of yellow to orange color. Their structures are fully confirmed by infrared, nmr, and ultraviolet spectra (see Figure 1).

Attempts to prepare 4′-bromo-3,5-di-*t*-butylfuchsone (IVd) by irradiation of an acetone solution of 4-bromobenzophenone (Id) and 2,6-di-*t*-butylphenol originally were unsuccessful. The only reaction product, formed in 37% yield, was 4″-bromo-4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (Vd). Only when the reaction was carried out in the presence of base could the bromosubstituted fuchsone IVd be isolated (see the Discussion).

4′,4″-Dihydroxy-3,5-di-*t*-butylfuchsone (IVj) was conveniently prepared by hydrolysis of 4′,4″-diacetoxy-3,5-di-*t*-butylfuchsone (IVi) rather than by direct photochemical reaction of 4,4′-dihydroxybenzophenone. Acid-catalyzed hydrolysis of IVi in the presence of zinc leads to 3,5-di-*t*-butyl-4,4′,4″-trihydroxytriphenylmethane (VI) (Scheme II).

Scheme II



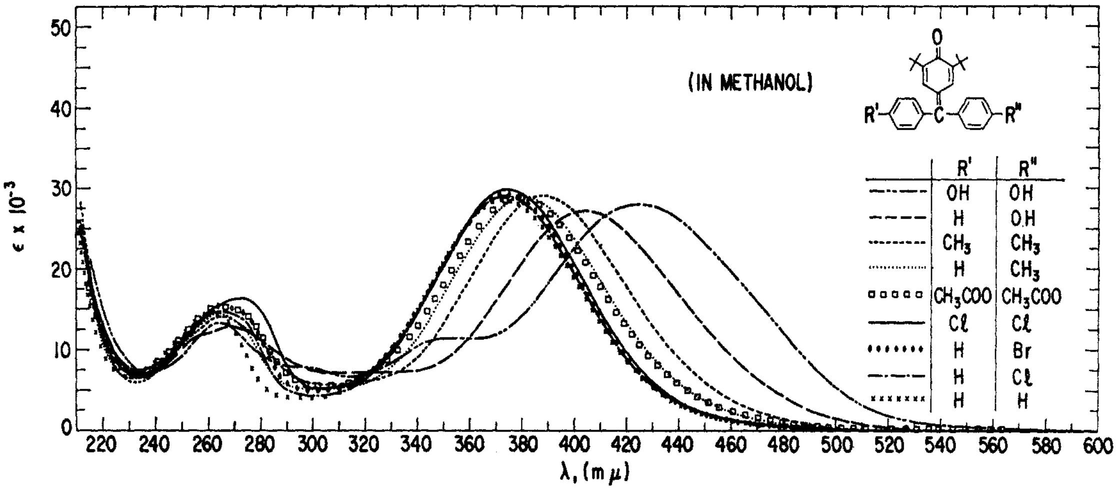
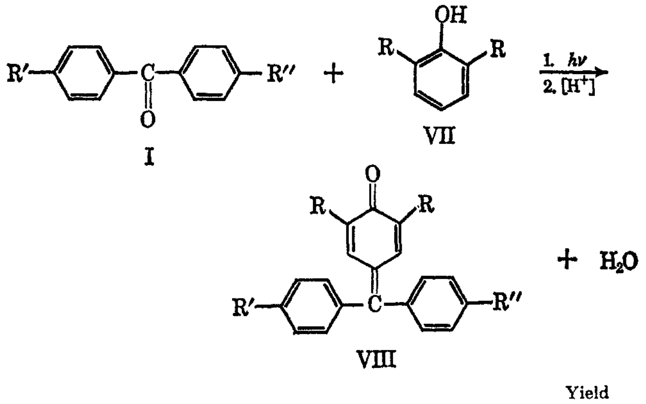


Figure 2.

2,6-Diisopropylphenol, 2,6-Dicyclohexylphenol, 2,6-Dimethoxyphenol, and 2,6-Dimethylphenol.—Other 2,6-disubstituted phenols, which in conventional oxidation reactions exhibit a behavior similar to that of 2,6-di-*t*-butylphenol, were chosen to be studied in the present investigation.

Irradiation of an acetone solution of benzophenone and 2,6-diisopropylphenol (VIIa), followed by acidification, yields 3,5-diisopropylfuchsone (VIIIa; see Table II) as bright yellow crystals.

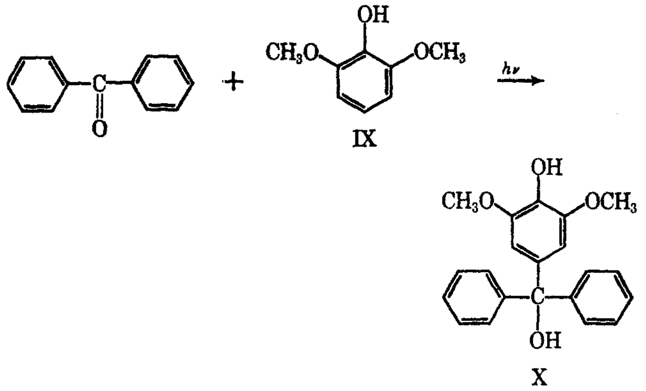
TABLE II



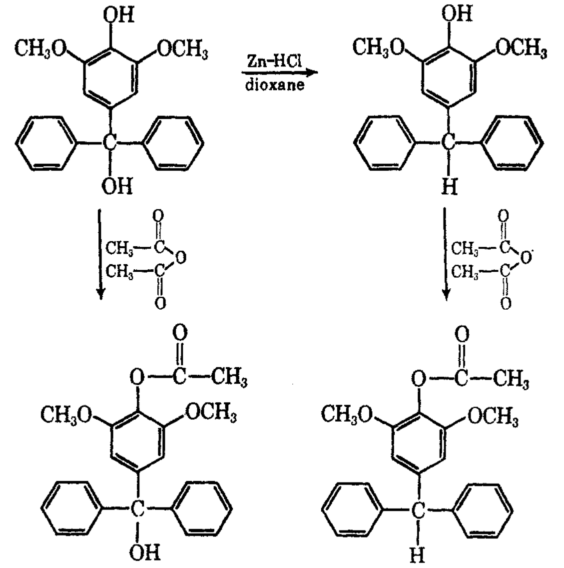
VII and VIII	R	R'	R''	Yield of VIII, %
a	Isopropyl	H	H	38
b	Cyclohexyl	H	H	34
c	Isopropyl	H	CH_3	40
d	Cyclohexyl	H	CH_3	52

In the same manner, 3,5-dicyclohexylfuchsone (VIIIb) is easily prepared from benzophenone and 2,6-dicyclohexylphenol (VIIb). Both phenols also react with photoexcited 4-methylbenzophenone yielding the quinone methides VIIIc and VIIId, respectively. The structures of fuchsones VIIIa–d are fully supported by infrared, nmr, and ultraviolet measurements (see Figure 2).

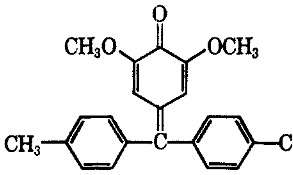
The photochemical reaction of benzophenone with 2,6-dimethoxyphenol (IX) in acetone solution leads to rapid precipitation of 3,5-dimethoxy-4-hydroxytriphenylcarbinol (X) isolated in analytically pure form—simply by filtration—in 68% yield. Chemical transformations of phenylcarbinol X are outlined in Scheme III.



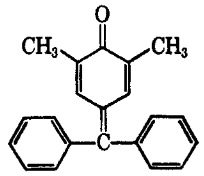
SCHEME III



Irradiation of 4,4'-dimethylbenzophenone in the presence of 2,6-dimethoxyphenol also results in the *para* coupling of the phenoxy radical with the ketyl radical. In this case, however, the corresponding 4-hydroxytriphenylcarbinol is soluble in acetone. Treatment of the reaction mixture with methanol slowly leads to the precipitation of 3,5-dimethoxy-4',4''-dimethylfuchsone VIIIe (15% yield).



VIIIe



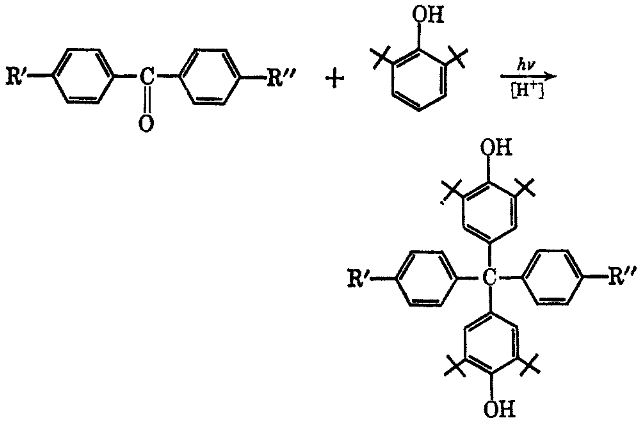
VIIIf

The photochemical reaction of benzophenone with 2,6-dimethylphenol was found to lead to a complex mixture of products from which only 3,5-dimethylfuchsone (VIIIf) was isolated in low yield.

B. Photochemical Formation of Tetraphenylmethanes.—After having ascertained the formation of quinone methides IV, the photochemical reaction of substituted benzophenones with 2,6-di-*t*-butylphenol in methanol in the presence of mineral acid was investigated.

By analogy to the formation of 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (Va; see Table III) described in the preceding paper, the one-step synthesis of tetraphenylmethanes Vb–h is easily accomplished by treating 2,6-di-*t*-butylphenol with the substituted benzophenones Ib–h. The yields are summarized in Table III.

Table III

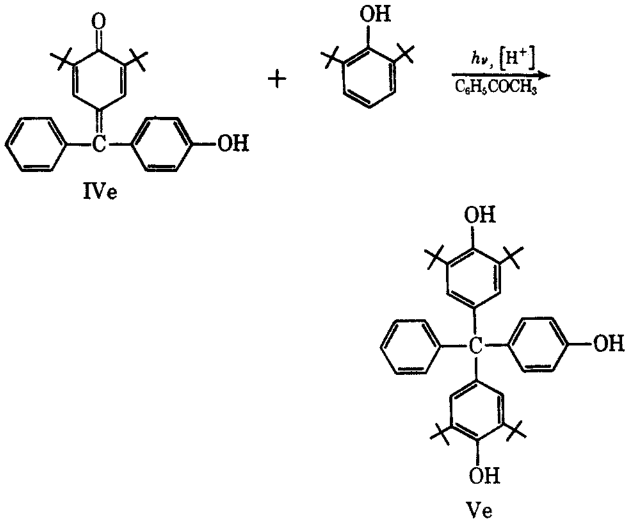


Va–h

I and V	R′	R″	Yield of V, %
a	H	H	65
b	H	CH_3	37
c	H	Cl	57
d	H	Br	55
e	H	OH	40
f	H	$COOCH_3$	57
g	CH_3	CH_3	20
h	Cl	Cl	35

The photochemical, acid-catalyzed reaction of 4,4′-diacetoxybenzophenone (Ii) with 2,6-di-*t*-butylphenol was carried out in acetic acid rather than in methanol in order to avoid complications due to ester solvolysis. The bisphenol (Vi) obtained in this reaction was not characterized as such but subsequently converted to 4,4′,4″,4‴-tetrahydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (Vj). The over-all yield of Vj, based on starting 4,4′-diacetoxybenzophenone, was 20% (Scheme IV).

Complications were encountered in the photochemical reaction of 4-hydroxybenzophenone with 2,6-di-*t*-butylphenol in acidified methanol or acetone solution. The tetraphenylmethane Ve was isolated in only 10 and 15% yields, respectively. A 40% yield of Ve, however, was obtained by adding 2,6-di-*t*-butylphenol in an acetophenone-sensitized reaction to 3,5-di-*t*-butyl-4′-hydroxyfuchsone IVe. This kind of photosensitized addition reaction was found to have general applicability and will be the subject of another paper.



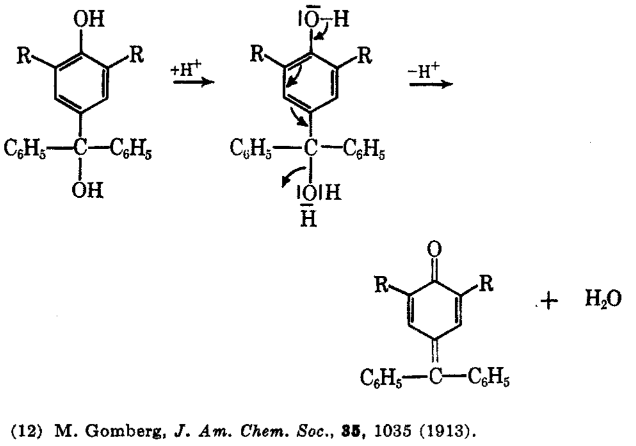
IVe

Ve

Discussion

On the basis of the discussion presented in the preceding paper, the photochemical reaction of substituted benzophenones with 2,6-disubstituted phenols in acetone solution can be interpreted by the sequence of reactions given in Scheme V.

The 2,6-disubstituted phenol was always applied in excess in order to avoid preferential attack of triplet-state benzophenone on the cyclohexadienone intermediate and the phenolic end product. In all irradiation experiments, however, the acetone solution sooner or later turned light yellow. Since 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol was found to eliminate water upon exposure to daylight in the solid state, and since it is known from the literature[12] that 4-hydroxytriphenylcarbinol is converted to fuchsone by sunlight, the yellow color appearing during the irradiation in acetone solution is probably to be attributed to quinone methide formation. This, however, means the formation of a photochemical quencher, having influence on the yields of 4-hydroxytriphenylcarbinols. Because of the high extinction coefficient of the quinone meth-



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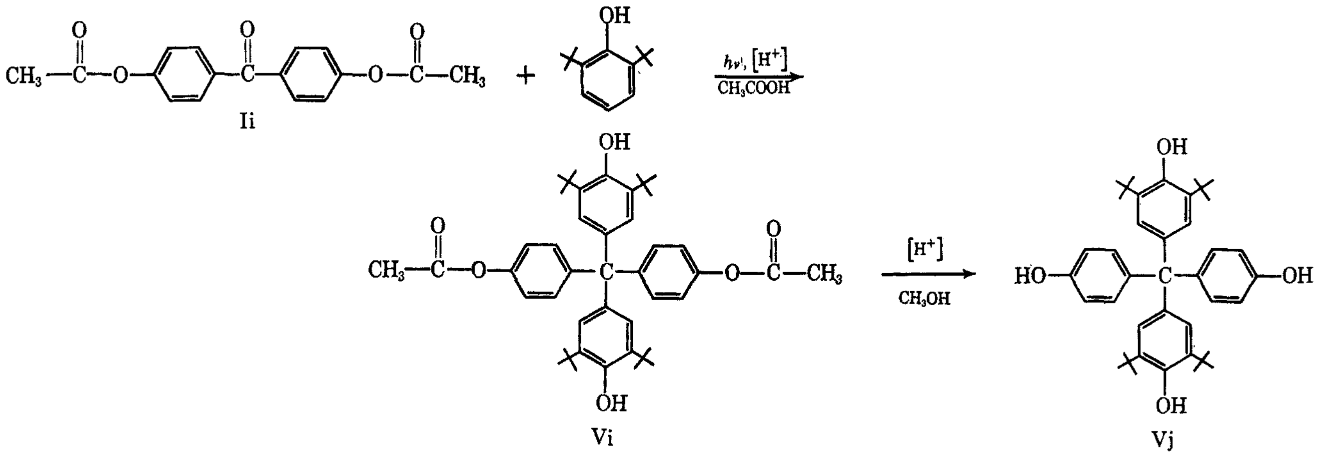
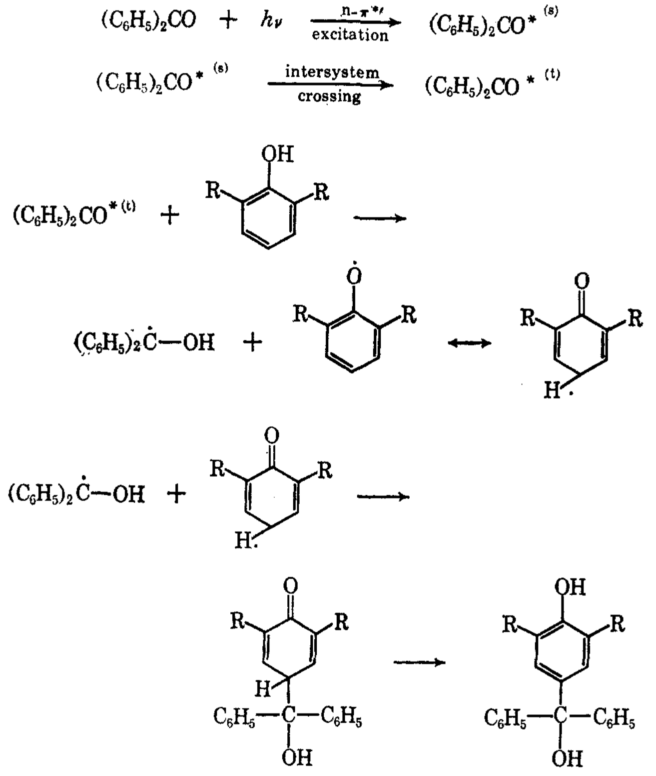
[12] M. Gomberg, *J. Am. Chem. Soc.*, **35**, 1035 (1913).

SCHEME IV



SCHEME V

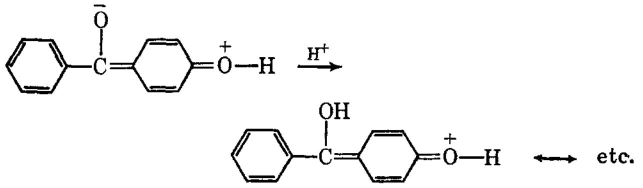


ides, much light is absorbed by this by-product. Furthermore, the portion of the light absorbed by benzophenone will not cause hydrogen abstraction from the phenol because of possible energy transfer from triplet-state benzophenone to the quinone methide. The nonphotochemical step—based on the elimination experiment of 3,5-di-*t*-butyl-4-hydroxytriphenylcarbinol described in the preceding paper—can be expected to proceed in high yield.

The photochemical decomposition of small amounts of 4′-bromo-3,5-di-*t*-butylfuchsone, formed already during the irradiation of 4-bromobenzophenone and 2,6-di-*t*-butylphenol in acetone solution, is probably responsible for the formation of 4″-bromo-4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (Vd). As it has been shown in the preceding paper, irradiation of 3,5-di-*t*-butylfuchsone at low concentrations does result in decomposition reactions, probably from the excited singlet state. Since HBr conceivably can be one of the decomposition products of the bromo-substituted fuchsone, the formation of Vd owing to the formation of a catalytic amount of HBr is not surprising. Thus, when the photochemical reaction of 4-bromobenzophenone with 2,6-di-*t*-butylphenol in acetone solution is carried out in the presence of ammonium hydroxide, then the fuchsone IVd can be isolated in good yield (65%).

As for the direct formation of bisphenols V from substituted benzophenones and 2,6-di-*t*-butylphenol, the continuation of the reaction sequence involving triplet energy transfer from benzophenone to the fuchsone, protonation of triplet state fuchsone followed by addition of 2,6-di-*t*-butylphenol, as discussed and experimentally supported in the preceding paper, can be applied here. All quinone methides described in this paper apparently are triplet energy acceptors as all substituted benzophenones employed are triplet energy donors in this system.

The low yield of Ve in the photochemical reaction of 4-hydroxybenzophenone with 2,6-di-*t*-butylphenol in acidified methanol and acidified acetone is well understood in the light of recent results obtained on the photopinacolization of 4-hydroxybenzophenone. In hydroxylic solvents 4-hydroxybenzophenone is known to exhibit a "charge transfer" band rather than an absorption due to an n–π^* transition generally required for photochemical hydrogen abstraction.[4] The presence of mineral acid could be the reason for the low yield of 3,3′,5,5′-tetra-*t*-butyl-4,4′,4″-trihydroxytetraphenylmethane (Ve) obtained by irradiating 4-hydroxybenzophenone and 2,6-di-*t*-butylphenol in acetone solution. It is conceivable that protonation leads to stabilization of the ionic resonance contributors of 4-hydroxybenzophenone, ineffective in the photochemical dehydrogenation reaction. The effect of protons on the photochemical reduction of benzophenones, however, remains to be studied in more detail. It has earlier been found that the rate of hydrogen transfer from isopropyl alcohol to photoexcited quinones decreases with increasing acidity.[13] This observation,



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(13) C. F. Wells, *Nature*, **177**, 483 (1956).

TABLE IV

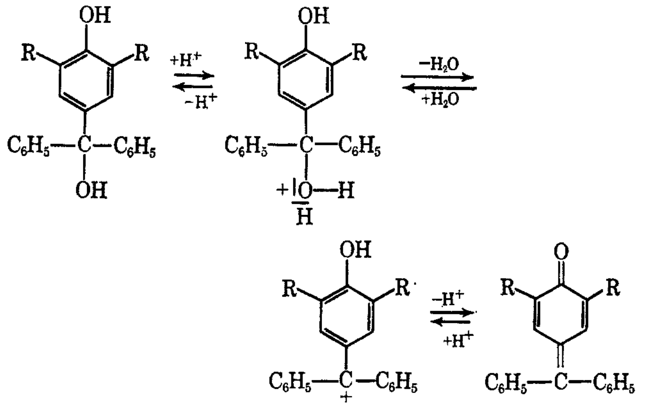
THE PHOTOCHEMICAL PREPARATION OF FUCHSONES

I (mmoles)	Phenol (mmoles)	Acetone, ml	Time, hr	Product	Yield, %	Mp, °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	Mol wt[a] Calcd	Mol wt[a] Found
c (5)	II (7.5)	55	4	IVc	52	201–202	$C_{27}H_{29}ClO$	80.08	80.30	7.22	7.17	404.99	413
d (5)	II (10)	75[b]	3	IVd	65	209–210	$C_{27}H_{29}BrO$	72.16	72.20	6.50	6.67	449.44	435
e (10)	II (20)	150	27	IVe	52	258–260[c]	$C_{27}H_{30}O_2$	83.90	84.04	7.82	7.78	386.54	383
f (5)	II (10)	60	5	IVf	54	187–188	$C_{29}H_{32}O_3$	81.27	81.46	7.53	7.52	428.55	400
g (5)	II (10)	100	10	IVg	41	195–196[d]	$C_{29}H_{34}O$	87.39	87.53	8.60	8.48	398.60	388
h (5)	II (10)	100	16	IVh	50	223–224	$C_{27}H_{28}Cl_2O$	73.80	73.84	6.42	6.47	439.43	429
i (5)	II (10)	75	11	IVi	63	262–263	$C_{31}H_{34}O_5$	76.52	76.59	7.04	7.21	486.62	465
a (10)	VIIa (20)	150	16	VIIIa	38	171–172	$C_{25}H_{26}O$	87.68	87.52	7.65	7.65	342.49	350
a (10)	VIIb (10)	60	11	VIIIb	34	238–240	$C_{31}H_{34}O$	88.10	88.29	8.11	8.11	422.62	422
b (5)	VIIa (10)	60	8	VIIIc	40	164–165	$C_{26}H_{28}O$	87.60	87.33	7.92	7.99	356.52	358
b (5)	VIIb (10)	60	4.5	VIIId	52	209–210	$C_{32}H_{36}O$	88.03	88.10	8.31	8.31	436.65	431

[a] All molecular weights were determined by thermoelectric measurement in benzene. [b] Containing 0.2 ml of concentrated ammonium hydroxide. [c] The substance first melts at 248–250°, turns yellow, and resolidifies. [d] The substance first melts at 190°, but resolidifies.

however, was interpreted in terms of the formation of unreactive oxonium ion, formed by protonation of the alcohol.

Attempts to prepare 4,4′-dihydroxytetraphenylmethanes by photochemical reaction of benzophenone in acidified methanol solution with 2,6-disubstituted phenols other than 2,6-di-*t*-butylphenol have been unsuccessful. As the photochemical experiments conducted in acetone solution in the absence of acid reveal, however, benzophenone does react with 2,6-disubstituted phenols to give 3,5-disubstituted 4-hydroxytriphenylcarbinols, which can eliminate water. However, apparently we are dealing with an equilibrium, which generally lies on the side of the 4-hydroxytriphenylcarbinol. Unsubstituted fuchsone (R = H) indeed has been described to add water in an acid-catalyzed reaction,[14] and it is known that protonation of 4-hydroxytriphenylcarbinol and protonation of fuchsone lead to the same carbonium ion.[15] The bulky *t*-butyl groups obviously enhance the collapse of the intermediate 4-hydroxytriphenylmethyl cation. In the reaction of 4-hydroxy-3,5-di-*t*-butyltriphenylcarbinol with mineral acid the equilibrium lies entirely on the side of 3,5-di-*t*-butylfuchsone, which is the key intermediate for the photochemical formation of the substituted tetraphenylmethane.



Experimental Section

The Apparatus.—All irradiations were carried out in an apparatus described in the preceding paper. 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 about 16° under nitrogen passed through a frit into the reaction mixture during irradiation.

Materials.—Phenols and benzophenones were either distilled or recrystallized before use. All melting points were taken on a Fisher-Johns melting point apparatus and are not corrected. All molecular weights were determined by thermoelectric measurement in benzene unless otherwise stated.

3,5-Di-*t*-butylfuchsone (IVa).—See the preceding paper for the preparation.

3,5-Di-*t*-butyl-4′-methylfuchsone (IVb).—A solution of 2,6-di-*t*-butylphenol (2.06 g, 10 mmoles) and 4-methylbenzophenone (980 mg, 5 mmoles) in acetone (100 ml) was irradiated for 5 hr. The light yellow solution was evaporated *in vacuo*, and the yellow, oily residue was dissolved in 20 ml of methanol, and acidified with 1 drop of concentrated hydrochloric acid dissolved in 1 ml of methanol. The yellow crystals thus formed were removed by filtration and recrystallized by dissolving in little chloroform and adding methanol (yield 1.1 g, 57%), mp 203–204°.

Anal. Calcd for $C_{28}H_{32}O$ (384.60): C, 87.45; H, 8.39. Found: C, 87.25; H, 8.49; mol wt, 379.

Experimental data on the preparation of other fuchsones (IVc–i and VIIIa–d) involving a similar work-up are listed in Table IV.

4,4′-Dihydroxy-3,5-di-*t*-butylfuchsone (IVj).—A suspension of 4′,4″-diacetoxy-3,5-di-*t*-butylfuchsone (2.43 g, 5 mmoles) in methanol (75 ml) containing concentrated hydrochloric acid (3 ml) was refluxed under stirring for 4 hr. The clear, deep red solution was concentrated by distilling off part of the solvent, and the orange precipitate thus obtained was recrystallized from boiling methanol (yield 2.0 g, 99%), mp 324–325°.

Anal. Calcd for $C_{27}H_{30}O_3$ (402.54): C, 80.56; H, 7.51. Found: C, 80.59; H, 7.68; mol wt (acetone), 422.

4,4′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (Va).—A solution of benzophenone (5.46 g, 35 mmoles) and 2,6-di-*t*-butylphenol (4.12 g, 20 mmoles) in methanol (60 ml) containing concentrated hydrochloric acid (0.1 ml) was irradiated for 19 hr. The colorless, crystalline precipitate was removed by filtration and heated with little boiling methanol in order to remove coprecipitated benzpinacol (yield 3.68 g, 64%), mp 235°. Recrystallization by dissolving in hot chloroform and adding 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).

Experimental data on the preparation of other tetraphenylmethanes (Vb–Vh) involving a similar work-up are listed in Table V.

3,3′,5,5′-Tetra-*t*-butyl-4,4′,4″-trihydroxytetraphenylmethane (Ve). By Acetophenone-Sensitized Addition of 2,6-Di-*t*-butylphenol to 3,5-Di-*t*-butyl-4′-hydroxyfuchsone.—A solution of IIIe (579 mg 1.5 mmoles), 2,6-di-*t*-butylphenol (412 mg, 2 mmoles), and acetophenone (12 g, 100 mmoles) in methanol (50 ml) containing 0.2 ml of concentrated hydrochloric acid was irradiated for 27 hr. By then the solution was light yellow. The solvent was removed *in vacuo* and the acetophenone was removed by dis-

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(15) K. I. Beynon and S. T. Bowden, *J. Chem. Soc.*, 4247 (1957).

TABLE V

PHOTOCHEMICAL PREPARATION OF TETRAPHENYLMETHANES

I	II	CH_3OH,	HCl,	Time,	Prod-	Yield,	Mp,		C, %		H, %		Mol wt[a]	
(mmoles)	(mmoles)	ml	ml	hr	uct V	%	°C	Formula	Calcd	Found	Calcd	Found	Calcd	Found
b (20)	b (10)	75	0.2	14	b	37	211–212	$C_{42}H_{54}O_2$	85.37	85.45	9.21	9.25	590.90	562
c (10)	c (10)	60	0.1	23	c	57	214–215	$C_{41}H_{51}ClO_2$	80.56	80.18	8.41	8.56	611.32	618
d (10)	d (10)	60	0.1	22	d	55	214–215[b]	$C_{41}H_{51}BrO_2$	75.10	75.15	7.84	7.86	655.78	639
e (20)[c]	e (10)	55	0.2	18	e[c]	10	259–260	$C_{41}H_{52}O_3$	83.06	82.87	8.84	8.64	592.82	588
f (10)[d]	f (10)	60	0.1	16	f	57	220–221	$C_{43}H_{54}O_4$	81.35	81.05	8.57	9.04	634.86	600
g (10)	g (5)	55	0.2	18	g	20	243–244	$C_{43}H_{56}O_2$	85.38	85.55	9.33	9.56	604.93	582
h (10)[d]	h (15)	80	0.2	18	h	35	244–245	$C_{41}H_{50}Cl_2O_2$	76.26	76.17	7.80	7.91	645.76	596

[a] All molecular weights were determined by thermoelectric measurement in benzene. [b] The substance first melts at 199° upon fast heating, solidifies again, and then melts at 214–215°. [c] For an additional experiment describing the preparation of Ve, see the Experimental Section. [d] Owing to its low solubility, the benzophenone was partially suspended in methanol.

tillation at about 1 mm. The solid residue was dissolved in 10 ml of methanol. Addition of few drops of water gave a light yellow, crystalline precipitate (yield, 560 mg), mp 255°. The substance was subjected to sublimation at 10 mm (bath temperature 140°), thus removing the small amount of yellow by-product. The remaining colorless, crystalline material was recrystallized from a little hot methanol (yield 350 mg, 40%), mp 259–260°.

Anal. Calcd for $C_{41}H_{52}O_3$ (592.87): C, 83.06; H, 8.84. Found: C, 82.87; H, 8.64; mol wt, 588.

4,4′,4″,4‴-Tetrahydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (Vj).—A solution of 4,4′-diacetoxybenzophenone (1.4 g, 5 mmoles) and 2,6-di-*t*-butylphenol (1.55 g, 7.5 mmoles) in acetic acid (60 ml) containing concentrated hydrochloric acid (0.03 ml) was irradiated for 28 hr. The colorless precipitate was removed from the mixture by filtration (crude yield 1.4 g), unsharp melting point around 200°. It was dissolved in a boiling mixture of methanol (30 ml) and concentrated hydrochloric acid (3 ml) and the solution was boiled for 10 min. Dilution with water gave a colorless precipitate which was recrystallized from a boiling mixture of chloroform and petroleum ether (bp 60–110°) (yield 610 mg, 20%), mp 288–289° dec.

Anal. Calcd for $C_{41}H_{52}O_4$ (608.87): C, 80.88; H, 8.61. Found: C, 80.98; H, 8.44; mol wt, 647.

3,5-Di-*t*-butyl-4,4′,4″-trihydroxytriphenylmethane (VI).—A suspension of 4′,4″-diacetoxy-3,5-di-*t*-butylfuchsone (2.43 g, 5 mmoles) in methanol (100 ml) and concentrated hydrochloric acid (10 ml) was treated with zinc dust (5 g) and refluxed until the reaction mixture was colorless. The reaction mixture was filtered, the filtrate was diluted with water, and the colorless precipitate thus obtained was recrystallized from aqueous methanol (yield 1.95 g, 96%), mp 241–242°.

Anal. Calcd for $C_{27}H_{32}O_3$ (404.56): C, 80.16; H, 7.97. Found: C, 80.33; H, 7.98; mol wt (chloroform), 458.

3,5-Dimethoxy-4″,4″-dimethylfuchsone (VIIIe).—A solution of 2,6-dimethoxyphenol (1.54 g, 10 mmoles) and 4,4′-dimethylbenzophenone (1.05 g, 5 mmoles) in acetone (100 ml) was irradiated for 16 hr. The yellow solution was evaporated and the brown, oily residue was dissolved in 30 ml of methanol. After 2 days crystals appeared in the dark, oily residue. The mixture was treated with a mixture of acetone and petroleum ether (bp 60–110°) and filtered. The yellow, crystalline material was recrystallized from hot chloroform by adding methanol (yield 250 mg 14.5%), mp 230°.

Anal. Calcd for $C_{23}H_{22}O_3$ (346.43): C, 79.74; H, 6.40. Found: C, 79.48; H, 6.45; mol wt, 345.

3,5-Dimethylfuchsone (VIIIf).—A solution of benzophenone (910 mg, 5 mmoles) and 2,6-dimethylphenol (1.22 g, 10 mmoles) in acetone (100 ml) was irradiated for 24 hr. Evaporation of the solvent left an oily residue from which excess 2,6-dimethylphenol was removed by vacuum sublimation. The remaining dark brown, oily substance was treated with methanol (after 2 months of standing in an open beaker), yielding 100 mg (7%) of orange-yellow crystals, mp 200–202°.

Anal. Calcd for $C_{21}H_{18}O$ (286.38): C, 88.08; H, 6.33. Found: C, 88.21; H, 6.23; mol wt, 291.

3,5-Dimethoxy-4-hydroxytriphenylcarbinol (X).—A solution of 2,6-dimethoxyphenol (1.54 g, 10 mmoles) and benzophenone (910 mg, 5 mmoles) in acetone (100 ml) was irradiated for 3.5 hr. The colorless precipitate which started forming about 30 min after irradiation began was then removed by filtration (yield 800 mg). Evaporation of the filtrate gave additional 350 mg of colorless crystals (total yield 1.15 g, 68%, mp 207–208° (lit.[15] 210–212°). The substance turns yellow upon heating to its melting point.

3,5-Dimethoxy-4-hydroxytriphenylmethane.—Zinc dust was added to the deep red solution of X (500 mg, 1.48 mmoles) in dioxane (20 ml) and concentrated hydrochloric acid (20 ml) until the color had faded. After addition of ether (50 ml) the reaction mixture was filtered. In the filtrate the reduction product crystallized in form of colorless needles (yield 410 mg, 81%), mp 132–133° (lit.[15] 131°).

4-Acetoxy-3,5-dimethoxytriphenylmethane.—A solution of 3,5-dimethoxy-4-hydroxytriphenylmethane (150 mg, 0.48 mmole) in a mixture of pyridine (5 ml) and acetic anhydride (5 ml) was refluxed for 5 min. Evaporation of the slightly yellow reaction mixture gave 140 mg (82%) of colorless crystals, mp 192–193°.

Anal. Calcd for $C_{23}H_{22}O_4$ (362.43): C, 76.22; H, 6.12; acetyl, 13.05. Found: C, 76.13; H, 6.42; acetyl, 13.07.

Spectra.[16]—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. Methanol was used as solvent. Proton magnetic resonance spectra were taken on a Varian A-60 spectrometer using deuteriochloroform solution with tetramethylsilane as internal standard.

Registry No.—IVa, 13131-76-5; IVb, 13134-98-0; IVc, 13134-99-1; IVd, 13135-00-7; IVe, 13135-01-8; IVf, 13127-37-2; IVg, 13135-02-9; IVh, 13127-38-3; IVi, 13135-03-0; IVj, 13135-04-1; Va, 13135-05-2; Vb, 13127-39-4; Vc, 13135-06-3; Vd, 13135-07-4; Ve, 13135-08-5; Vf, 13135-09-6; Vg, 13127-40-7; Vh, 13169-21-6; Vj, 13127-41-8; VI, 13127-42-9; VIIIa, 13135-10-9; VIIIb, 13127-43-0; VIIIc, 13135-11-0; VIIId, 13127-44-1; VIIIe, 13135-12-1; VIIIf, 13135-13-2; 4-acetoxy-3,5-dimethoxytriphenylmethane, 13135-14-3.

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