

Thermal and Photochemical Addition Reactions of Organosilicon Hydrides

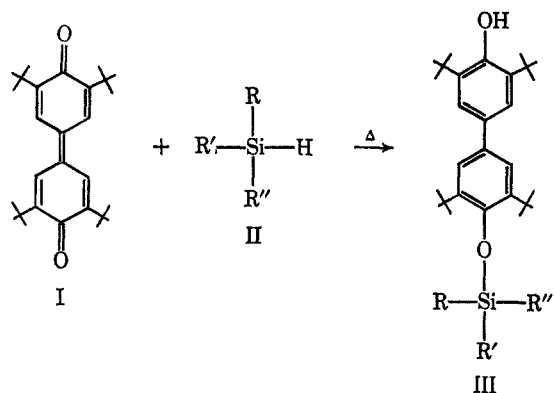
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Phenylsilicon hydrides react with benzophenone at elevated temperature, yielding alkoxy silicon compounds by 1,2 addition to the carbonyl group.¹ The addition of organosilicon hydrides to quinones, however, apparently has not been reported yet. Therefore, and in view of a recent report² on the thermal dehydrogenation of diphenylmethane by 3,3',5,5'-tetra-*t*-butyldiphenoquinone (I), it appeared interesting to study the reaction of tetra-*t*-butyldiphenoquinone with some phenylsilicon hydrides.

We have now found that diphenylsilane (IIa) upon heating to 275° smoothly reacts with 3,3',5,5'-tetra-*t*-butyldiphenoquinone to give the monodiphenylsilyl ether of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenyl (IIIa) in 80% yield. Triphenylsilane and tribenzylsilane add to the diphenoquinone I in the same manner,

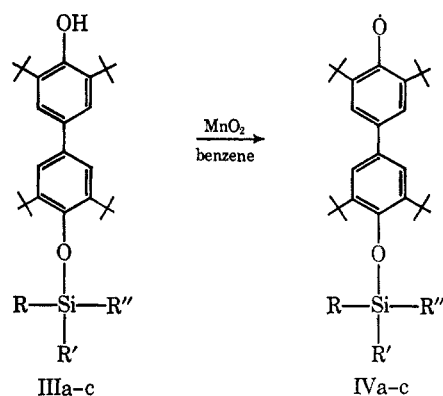


IIa and IIIa, R = H; R' = C₆H₅; R'' = C₆H₅
 IIb and IIIb, R = C₆H₅; R' = C₆H₅; R'' = C₆H₅
 IIc and IIIc, R = C₆H₅CH₂; C₆H₅CH₂; C₆H₅CH₂

giving the monosilyl ethers IIIb and IIIc in 69 and 30% yield, respectively.

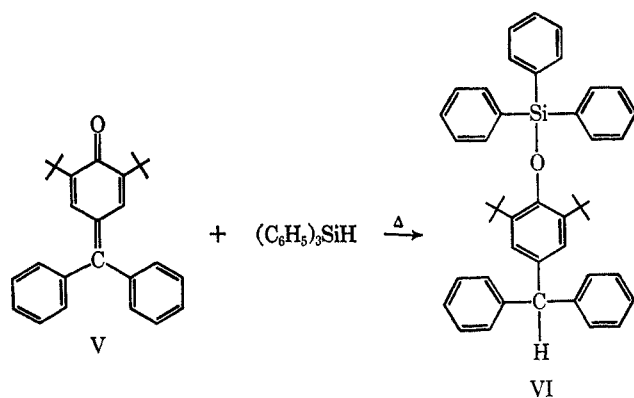
The structure of the addition products III is confirmed by analytical and nuclear magnetic resonance (nmr) spectroscopic data. Figure 1 shows the increasing effect of magnetic shielding of one pair of *t*-butyl groups due to the proximity of phenyl rings.

Oxidation of the sterically hindered phenols IIIa-c with active manganese dioxide³ in benzene solution leads in quantitative yield to deep blue or purple phenoxy radicals IV which were isolated by freeze-



drying technique. The electron spin resonance (esr) spectra of IVa-c (in benzene) show an unresolved triplet having a peak to peak line width of about 5 G.

Thermal addition of phenylsilanes was also found to be applicable to other compounds with quinoid structure. Thus, the reaction of triphenylsilane with the quinone methide 3,5-di-*t*-butylfuchsone (V), at 330° re-



sults in a 1,6 addition, giving the triphenylsilyl ether of 3,5-di-*t*-butyl-4-hydroxytriphenylmethane (VI).

Ultraviolet (uv) irradiation of triphenylsilane in acetone solution reportedly yields the triphenylsilyl ether of isopropyl alcohol.⁴ The photochemical reaction of benzophenone with triphenylsilane, however, has not previously been investigated. (The statement⁵ that benzophenone does not react photochemically with triphenylsilane seems to be due to an error in translation.) We find that irradiation of a solution of benzophenone and triphenylsilane in benzene, using uv light filtered through Pyrex, results in the rapid formation of the monotriphenylsilyl ether of benzopinacol (VII), isolated in 56% yield. The structure

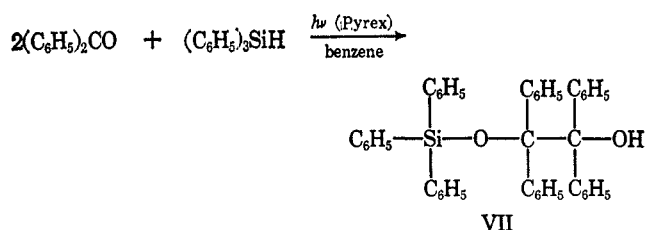
(3) Cf. H.-D. Becker, *J. Org. Chem.*, **29**, 3068 (1964). Oxidation of 2,4,6-tri-*t*-butylphenol with active manganese dioxide in the presence of other phenols is known to lead to quinol ethers. An attempt to prepare a quinol ether by oxidation of IIIa with active manganese dioxide in the presence of 4-hydroxydiphenylthio ether, however, resulted in the formation of 3,3',5,5'-tetra-*t*-butyldiphenoquinone, conceivably involving the hydrolysis of an intermediate quinone ketal.

(4) R. Calas and N. Duffaut, *C. R. Acad. Sci., Paris*, **245**, 906 (1957).

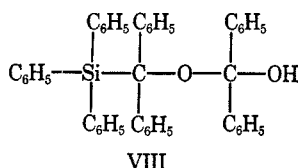
(5) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960, p 213.

(1) H. Gilman and D. Wittenberg, *J. Org. Chem.*, **23**, 501 (1958).

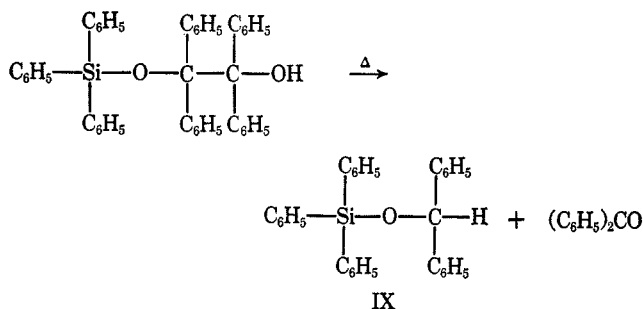
(2) A. S. Hay, *Tetrahedron Lett.*, No. 47, 4241 (1965).



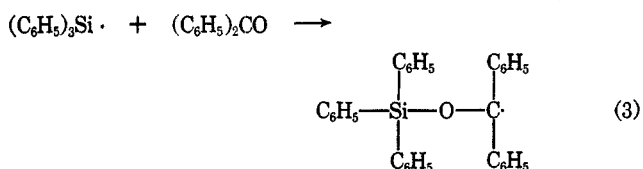
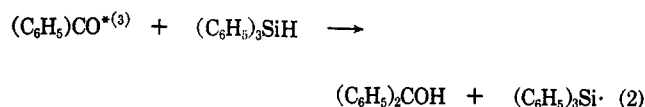
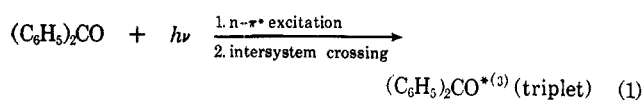
of VII is based on analytical, infrared (ir), and nmr spectroscopic data. The possible isomeric structure VIII is excluded on the basis of the stability of the 2:1



addition product of benzophenone to triphenylsilane toward 2,4-dinitrophenylhydrazine in acidified (H_2SO_4) ethanol.⁶ Analogous to the behavior of benzopinacol, upon heating to its melting point, VII smoothly decomposes into the triphenylsilyl ether of benzhydrol IX and benzophenone.⁷

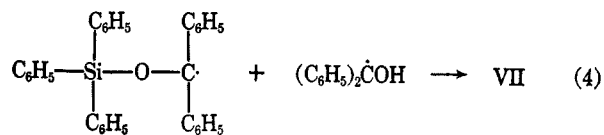


The mechanism of the photochemical formation of VII conceivably involves hydrogen abstraction from triphenylsilane by triplet-state benzophenone to give a ketyl radical and a triphenylsilyl radical (eq 1 and 2). Addition of the silyl radical to ground-state benzophenone and coupling of the ketyl radical with the thus formed carbon radical then leads to the monotriphenylsilyl ether of benzopinacol (eq 3 and 4). It



(6) The 2,4-dinitrophenylhydrazine solution was prepared according to "The Systematic Identification of Organic Compounds," by R. L. Shriner, R. C. Fuson, and D. Y. Curtin, Fourth ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 219.

(7) Cf. A. G. Brook, *J. Amer. Chem. Soc.*, **80**, 1886 (1958).



is worth noting that the 2:1 addition product was also formed as the sole product when benzophenone was used in deficiency.

Experimental Section

All melting points were taken on a Fisher-Johns melting point apparatus and are not corrected.

Molecular weights were determined by thermoelectric measurement in benzene.

Addition of Diphenylsilane to 3,3',5,5'-Tetra-*t*-butyldiphenylquinone (IIIa).—A suspension of tetra-*t*-butyldiphenylquinone (3.05 g, 7.5 mmol) in diphenylsilane (20 ml) was heated under nitrogen to 270–275° whereupon a colorless solution was formed. Diphenylsilane was then removed by vacuum distillation [bp 75° (1 mm)]. The remaining colorless residue was distilled at 1-mm pressure (bp 250–255°) giving 3.54 g (80%) of the monodiphenylsilyl ether of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenyl as a colorless liquid which formed a glass at room temperature.

Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Si}$ (592.95): C, 81.03; H, 8.84. Found (565): C, 80.91; H, 9.02.

Addition of Triphenylsilane to 3,3',5,5'-Tetra-*t*-butyldiphenylquinone (IIIb).—Tetra-*t*-butyldiphenylquinone (2.04 g, 5 mmol) was added to triphenylsilane (5 g) at 250° and the solution was heated for 15 min under nitrogen at 300–310°. Excess triphenylsilane was then removed by vacuum distillation at 1-mm pressure and a bath temperature of 220°. The glassy residue was subjected to vacuum sublimation under the same conditions, giving 2.3 g (69%) of monotriphenylsilyl ether of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenyl as a partly colorless, crystalline (mp ~90°), partly light yellowish glassy sublimate.

Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_2\text{Si}$ (669.05): C, 82.58; H, 8.44. Found (641): C, 82.46; H, 8.33.

Addition of Tribenzylsilane to 3,3',5,5'-Tetra-*t*-butyldiphenylquinone (IIIc).—A mixture of tetra-*t*-butyldiphenylquinone (2.04 g, 5 mmol) and tribenzylsilane (5.5 g) was heated to 295–300° under nitrogen for 15 min until the dark solution had turned light yellow. The reaction mixture was then subjected to vacuum distillation at 1-mm pressure and a bath temperature of 230–240° to remove excess tribenzylsilane (3.8 g). The glassy residue was triturated with 10 ml of petroleum ether (bp 30–60°) and kept refrigerated overnight, yielding 1.06 g (30%) of the monotribenzylsilyl ether of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butyldiphenyl as colorless crystals, mp 165–170°.

Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{O}_2\text{Si}$ (711.13): C, 82.76; H, 8.79. Found (707): C, 82.77; H, 8.68.

Oxidation of IIIb with Active Manganese Dioxide to Give IVb.—Active manganese dioxide (10 g) was added under nitrogen to a solution of IIIb (1.0 g) in benzene (100 ml) placed in a screw-cap bottle. The suspension was shaken for 15 min and then filtered through a sintered-glass funnel. The manganese dioxide was washed with 25 ml of benzene and the deep blue filtrate was subjected to freeze drying. The dark blue solid residue (960 mg, 96%) melted between 100 and 110°.

Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_2\text{Si}$ (668.04): C, 82.71; H, 8.30. Found: C, 82.68; H, 8.39.

Oxidation of IIIa to give IVa was carried out in the same manner as that described above. Radical IVa formed a deep purple solid melting ~80° under decomposition.

Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{Si}$ (591.94): C, 81.16; H, 8.68. Found: C, 80.82; H, 8.56.

Oxidation of IIIc to give IVc was carried out in the same manner as described above for IIIb. Radical IVc formed a deep blue-green solid, melting between 65 and 70°.

Anal. Calcd for $\text{C}_{29}\text{H}_{31}\text{O}_2\text{Si}$ (710.12): C, 82.88; H, 8.66. Found: C, 82.50; H, 8.04.

Addition of Triphenylsilane to 3,5-Di-*t*-butylfuchsonone (VI).—A mixture of 3,5-di-*t*-butylfuchsonone (1.11 g, 3 mmol) and triphenylsilane (2 g, 7.7 mmol) was heated under nitrogen at 330–340° for 5 min. The almost colorless reaction mixture was dissolved in about 5 ml of ether and then diluted with 15 ml of

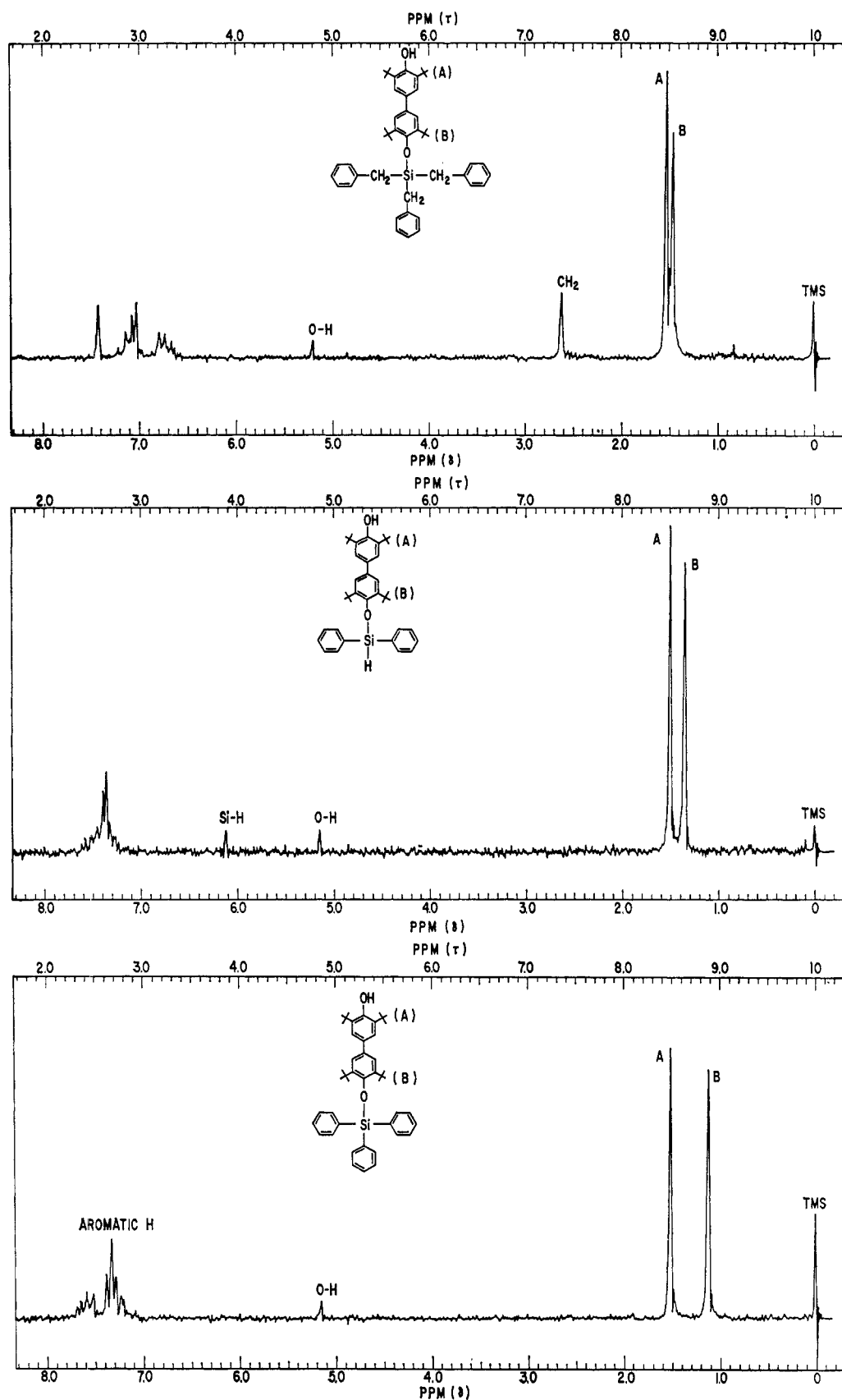


Figure 1.

methanol. After 3 hr, a colorless crystalline precipitate was removed by filtration, dissolved in 5 ml of ether, and filtered to remove traces of insoluble material. The ether filtrate was diluted with 50 ml of methanol, yielding colorless crystals, mp 130–131°, yield 850 mg (45%).

Anal. Calcd for $C_{18}H_{16}OSi$ (630.90): C, 85.66; H, 7.35. Found (623): C, 85.58; H, 7.49.

Photochemical Reaction of Benzophenone with Triphenylsilane to Give VII.—A solution of benzophenone (3.64 g, 20 mmol) and triphenylsilane (2.62 g, 10 mmol) in benzene (60 ml) was irradiated under nitrogen at 16° for 3.5 hr, using a water-cooled immersion well and a 100-W GE mercury lamp, type H 100 A4/T. The solvent was then evaporated *in vacuo* and the sticky, very light yellowish residue was dissolved in 50 ml of ether. The

ether solution was kept standing for 3 hr. The colorless crystalline precipitate formed during that period was removed by filtration: yield 3.5 g (56%), mp 129–131°. The substance can be recrystallized by dissolving it in little chloroform and adding methanol, thus raising the melting point to 132–133° dec.

Anal. Calcd for $C_{44}H_{36}O_2Si$ (624.87): C, 84.58; H, 5.81. Found (637): C, 84.57; H, 6.00.

Thermal Decomposition of VII.—The monotriphenylsilyl ether of benzopinacol (VII, 625 mg, 1 mmol) placed in a sublimator was heated for 15 hr at 95° *in vacuo* (10 mm). The crystalline sublimate was identified as benzophenone (mp 44–45°; mixture melting point with authentic material showed no depression): yield 180 mg (98%). The infrared (ir) spectrum of the glassy residue (molten between plates) was identical with that of the authentic thermal addition product of benzophenone and triphenylsilane.

Spectra.—Ir spectra were obtained with a Perkin-Elmer grating infrared spectrophotometer, Model 521. Nmr spectra were taken on a Varian A-60 spectrometer.

Registry No.—IIIa, 19886-70-5; IIIb, 19886-71-6; IIIc, 19886-72-7; IVa, 19886-73-8; IVb, 19886-74-9; IVc, 19886-75-0; VI, 19886-76-1; VII, 18862-02-7.

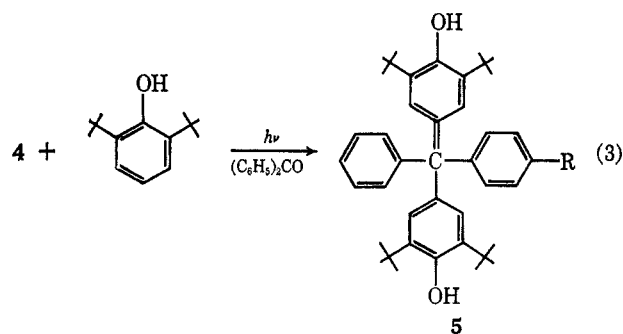
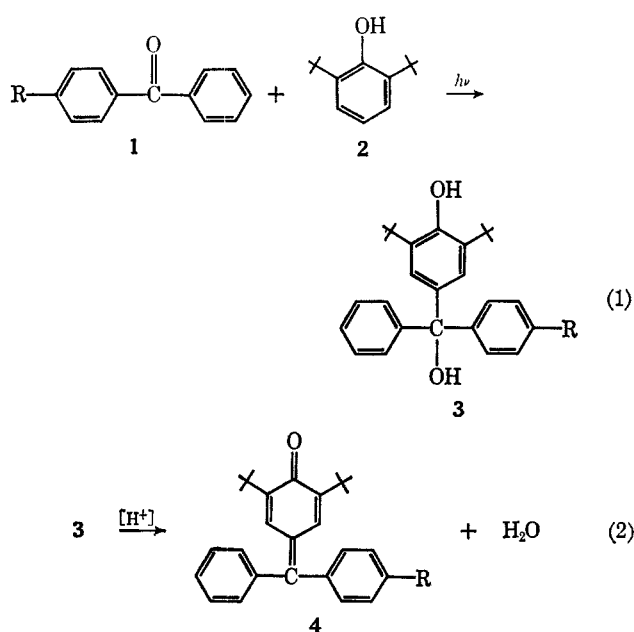
On the Photosensitized Reduction and Addition Reactions of Quinoid Compounds¹

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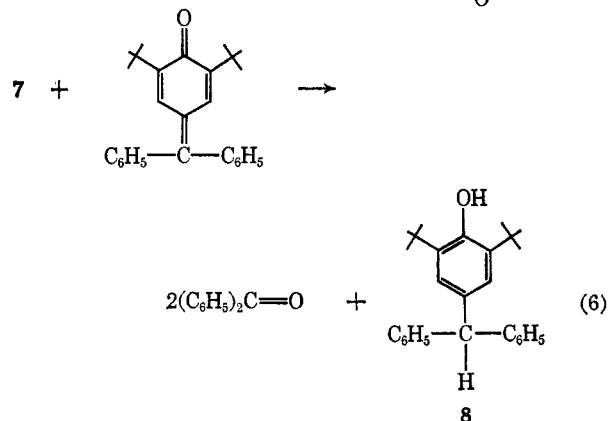
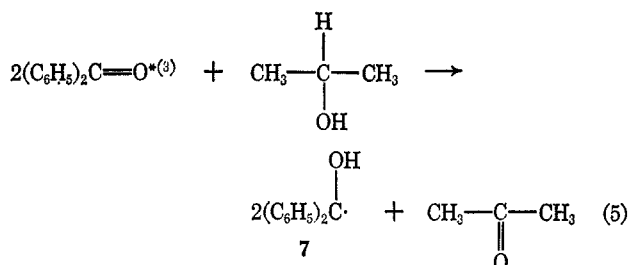
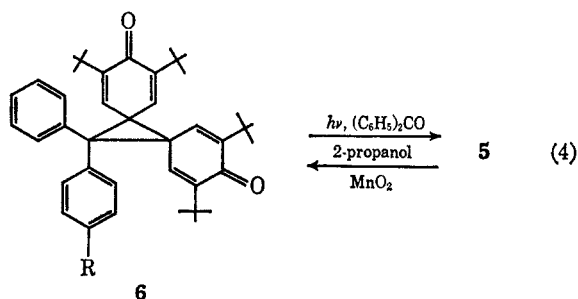
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Recently we described the photochemical reaction of benzophenone 1 ($R = H$) with 2,6-di-*t*-butylphenol 2 leading to bisphenol 5 ($R = H$) *via* intermediates 3 and 4 according to reactions 1–3.² It was suggested that a triplet energy transfer from photoexcited benzophenone to quinone methide 4 was involved in the addition reaction 3 of phenol 2.



Support for the energy-transfer reaction was deduced from the observation that irradiation of benzophenone in 2-propanol solution containing quinone methide 4 ($R = H$) did not lead to benzopinacol but resulted in the smooth reduction of the quinone methide. Acetophenone was found to sensitize the reduction in the same manner. During a subsequent investigation³ we also observed the benzophenone-sensitized reduction of bispirodienone 6 ($R = H$) in 2-propanol solution to give bisphenol 5 ($R = H$) (eq 4). Although these reductions appeared well explained by an energy-transfer reaction from benzophenone, the involvement of ketyl radicals 7 as outlined for the benzophenone-sensitized formation of 3,5-di-*t*-butyl-4-hydroxytriphenylmethane 8 was considered in a possible alternative mechanism⁴ (eq 5 and 6).



(1) Photochemical Reactions with Phenols. VI. For part V, see H.-D. Becker, *J. Org. Chem.*, **32**, 2140 (1967).

(2) H.-D. Becker, *ibid.*, **32**, 2115 (1967).

(3) H.-D. Becker, *ibid.*, **32**, 2136 (1967).

(4) A similar mechanism has been proposed earlier for the photochemical reduction of a pyrazolone azomethine dye: W. F. Smith and B. R. Rossiter, *J. Amer. Chem. Soc.*, **89**, 717 (1967).