

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.

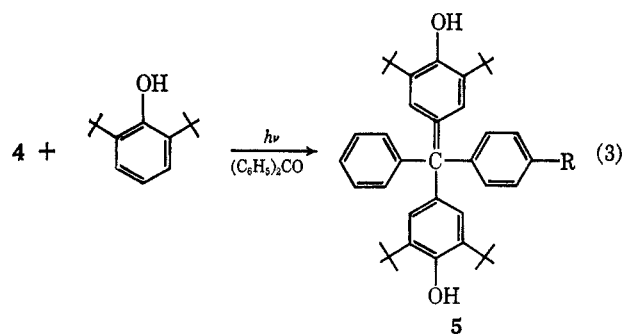
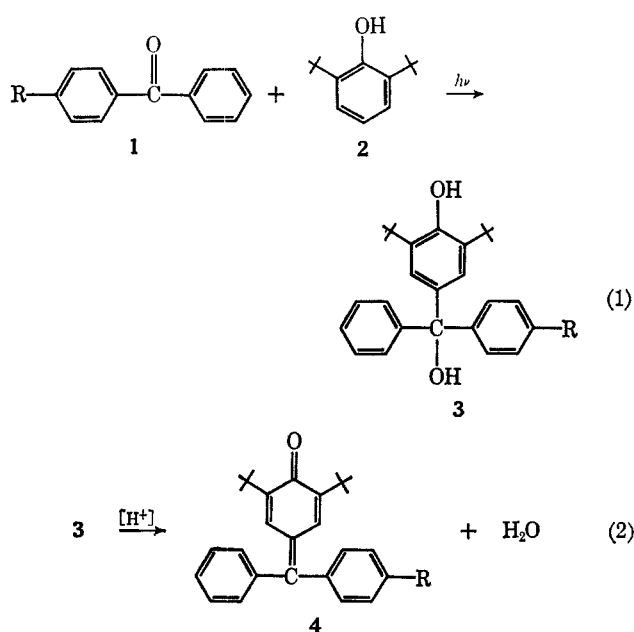
### On the Photosensitized Reduction and Addition Reactions of Quinoid Compounds<sup>1</sup>

HANS-DIETER BECKER

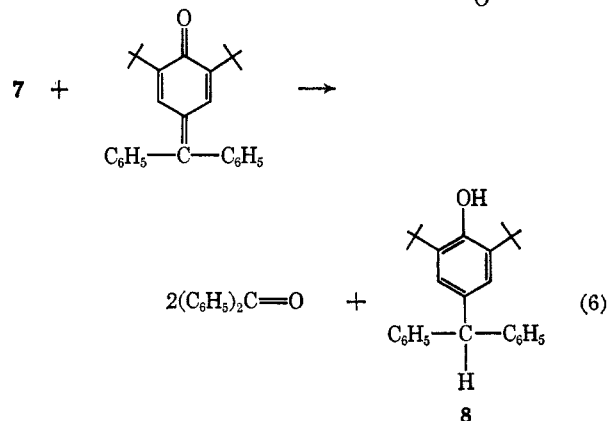
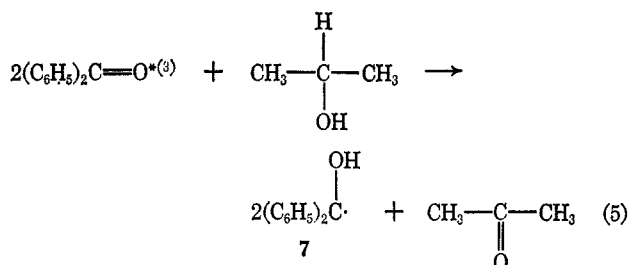
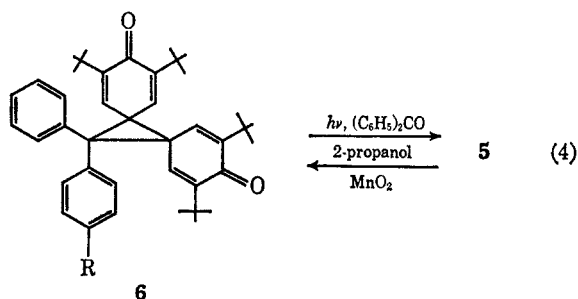
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Recently we described the photochemical reaction of benzophenone 1 ( $R = H$ ) with 2,6-di-*t*-butylphenol 2 leading to bisphenol 5 ( $R = H$ ) *via* intermediates 3 and 4 according to reactions 1–3.<sup>2</sup> It was suggested that a triplet energy 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 investigation<sup>3</sup> 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 mechanism<sup>4</sup> (eq 5 and 6).



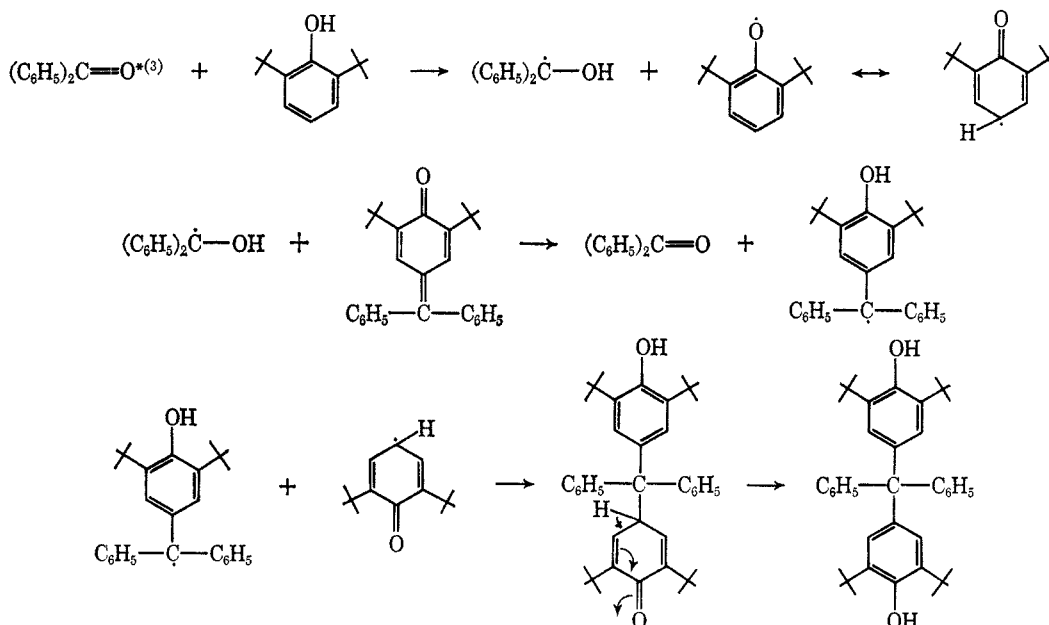
(1) Photochemical Reactions with Phenols. VI. For part V, see H.-D. Becker, *J. Org. Chem.*, **32**, 2140 (1967).

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

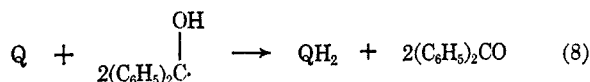
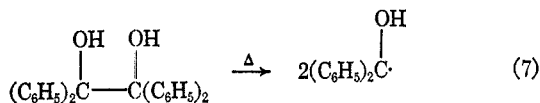
(3) H.-D. Becker, *ibid.*, **32**, 2136 (1967).

(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).

SCHEME I



A recent report<sup>5</sup> on reactions of diphenylhydroxymethyl radicals formed by thermal dissociation of benzpinacol has prompted us to examine the validity of this mode of reduction. We have now found that quinoid compounds Q indeed are easily reduced to  $\text{QH}_2$  by diphenylhydroxymethyl radicals generated by this non-photochemical method (eq 7 and 8). Thus, heating a



solution of quinone methide **4** ( $\text{R} = \text{H}$ ) (1 mmol) in the presence of an equimolar amount of benzpinacol in dimethylformamide to  $160^\circ$  for 3 min smoothly leads to 3,5-di-*t*-butyl-4-hydroxytriphenylmethane which was isolated in 92% yield. Bispirodienone **6** ( $\text{R} = \text{H}$ ) was reduced in the same manner giving bisphenol **5** ( $\text{R} = \text{H}$ ) in 97% yield. Likewise, heating a solution of 3,3',5,5'-tetra-*t*-butyldiphenylquinone in the presence of an equimolar amount of benzpinacol results in the smooth formation of 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl (97% yield).

In view of these findings, the photosensitized reduction of quinone methide **4** and bispirodienone **6** most likely does not involve the previously<sup>2,3</sup> proposed triplet energy-transfer reaction, but proceeds *via* diphenylhydroxymethyl radicals and dimethylhydroxymethyl radicals. Furthermore, the earlier<sup>2,6</sup> invoked energy-transfer mechanism for the photosensitized addition of phenols to quinone methides now seems doubtful. More likely, the role of benzophenone or acetophenone in the addition reaction (3) also is that of a hydrogen carrier as outlined in Scheme I. The previously described advantageous effect of protons on the addition reaction conceivably consists in the acid catalysis of the tautomerization step.

The photosensitized addition to quinone methides has been found to proceed smoothly only with 2,6-disubstituted phenols, suggesting that the lifetime of the corresponding phenoxy radicals may be of importance. Also, the generation of the phenoxy radicals must be a very efficient reaction since these addition reactions do proceed in alcohol solution, including 2-propanol, considered to be an excellent hydrogen donor. It is worth noting, however, that even 4-phenylbenzophenone (**1**,  $\text{R} = \text{phenyl}$ ) which is known<sup>7</sup> to abstract hydrogen atoms very inefficiently from 2-propanol reacts smoothly with 2,6-di-*t*-butylphenol as a hydrogen donor. Thus, irradiation of 4-phenylbenzophenone in acetone solution in the presence of 2,6-di-*t*-butylphenol and subsequent acidification gives 3,5-di-*t*-butyl-4'-phenylfuchsonone (**4**,  $\text{R} = \text{phenyl}$ ) in 63% yield, besides a minor amount of 4-phenylbenzophenonepinacol (7.7% yield). The photochemical reaction of 4-phenylbenzophenone with 2,6-di-*t*-butylphenol in acidified methanol results in the smooth formation of 4,4'-dihydroxy-4''-phenyl-3,3',5,5'-tetra-*t*-butyltetraphenylmethane (**5**,  $\text{R} = \text{phenyl}$ ), which was isolated in 53% yield. 4-Phenylbenzophenonepinacol was isolated in 15% yield. The structure of **5** ( $\text{R} = \text{phenyl}$ ) is confirmed by elemental analysis, molecular weight determination, spectroscopic data (ir and nmr), and its oxidative conversion into bispirodienone **6** ( $\text{R} = \text{phenyl}$ ).

The photochemical formation of **5** according to reactions 1-3 indicates that dimerization and coupling reactions of diphenylhydroxymethyl radicals are suppressed in the presence of quinoid compounds, apparently because the hydrogen atom transfer reaction as outlined in Scheme I is a highly efficient competing process.

#### Experimental Section

The photochemical reactions were carried out in a previously described immersion well apparatus.<sup>2</sup> Melting points were taken on a hot-stage microscope. Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(5) D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

(6) H.-D. Becker, *ibid.*, **32**, 2131 (1967).

(7) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

Molecular weights were determined by thermoelectric measurement.

**Reduction of Bispirodienone 6 (Standard Procedure).**—A solution of bispirodienone 6 ( $R = H$ )<sup>2</sup> (575 mg, 1 mmol) and benzopinacol (400 mg, 1.09 mmol) in dimethylformamide (6 ml) was kept at 160° for 3 min. Addition of water to the colorless solution gave a crystalline precipitate of bisphenol 5 ( $R = H$ ): yield 560 mg (97%); mp 233–234°. The mixture melting point with authentic<sup>2</sup> material was not depressed.

**3,5-Di-*t*-butyl-4'-phenylfuchsonone (4,  $R = Phenyl$ ).**—A solution of 4-phenylbenzophenone (1,  $R = phenyl$ ) (1.29 g, 5 mmol) and 2,6-di-*t*-butylphenol (2.06 g, 10 mmol) in acetone (60 ml) was irradiated (GE 100-W AH/4) under nitrogen for 4 hr. Vacuum evaporation of solvent from the light yellow reaction mixture gave an oily residue from which 100 mg (7.7%) of 4-phenylbenzophenonepinacol, mp 193–195°, was removed by filtration after treatment with 10 ml of methanol. Upon acidification of the methanol filtrate with 1 drop of concentrated hydrochloric acid dissolved in 1 ml of methanol, the yellow-orange 3,5-di-*t*-butyl-4'-phenylfuchsonone precipitated. It was removed by filtration and recrystallized from a boiling chloroform-methanol mixture: yield 1.42 g (63%); mp 192–193°; uv spectrum (in  $CH_3OH$ )  $\lambda_{max}$  283 m $\mu$  ( $\epsilon$  19,000), 387 (31,500).

*Anal.* Calcd for  $C_{33}H_{34}O$ : C, 88.74; H, 7.67; mol wt, 446.64. Found: C, 88.80; H, 7.77; mol wt (in benzene), 438.

**4,4'-Dihydroxy-4''-phenyl-3,3',5,5'-tetra-*t*-butyltetraphenylmethane (5,  $R = Phenyl$ ).**—A suspension of 4-phenylbenzophenone (1.29 g, 5 mmol) in a solution of 2,6-di-*t*-butylphenol (1.54 g, 7.5 mmol) in methanol (65 ml) containing hydrochloric acid (0.1 ml) was irradiated under nitrogen for 3 hr (Philips HPK, 125 W). A colorless precipitate formed as the benzophenone dissolved during the reaction. Partial vacuum evaporation of the solvent gave 1.7 g of crystalline residue. It was treated with 200 ml of boiling methanol. Hot filtration gave 200 mg (15%) of methanol-insoluble 4-phenylbenzophenonepinacol, mp 198–199° (lit.<sup>8</sup> mp 198–199°).

*Anal.* Calcd for  $C_{38}H_{30}O_2$ : C, 88.00; H, 5.83; mol wt, 518.62. Found: C, 87.85; H, 5.82.

After partial vacuum evaporation of the solvent from the filtrate crystalline bisphenol 5 ( $R = phenyl$ ) precipitated: yield 1.3 g (53%); mp 169–170°.

*Anal.* Calcd for  $C_{47}H_{36}O_2$ : C, 86.45; H, 8.65; mol wt, 652.92. Found: C, 86.31; H, 8.82; mol wt (in acetone), 610.

**Oxidation of 4,4'-Dihydroxy-4''-phenyl-3,3',5,5'-tetra-*t*-butyltetraphenylmethane (6,  $R = Phenyl$ ).**—A suspension of active manganese dioxide<sup>9</sup> (6.5 g) in a solution of 5 ( $R = phenyl$ ) (652 mg, 1 mmol) in benzene (50 ml) was shaken for 30 min. Filtration and vacuum evaporation of the filtrate gave a solid orange residue which was recrystallized by dissolving it in a little warm benzene and adding methanol: yield 600 mg (92%); mp 240–250° dec; ir spectrum (in KBr), no OH absorption, cyclohexadienone absorption at 1620–1645  $cm^{-1}$ .

*Anal.* Calcd for  $C_{47}H_{34}O_2$ : C, 86.72; H, 8.36; mol wt, 650.90. Found: C, 86.56; H, 8.36; mol wt (in benzene), 639.

**Registry No.**—4 ( $R = Ph$ ), 19886-68-1; 5 ( $R = Ph$ ), 19886-69-2; 6 ( $R = Ph$ ), 19922-48-6.

(8) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

(9) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. N. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

### The Action of Triethyl Phosphite on 1,5-Diphenyl-3-methyl-4-nitrosopyrazole. A Novel Cleavage of the Pyrazole Ring

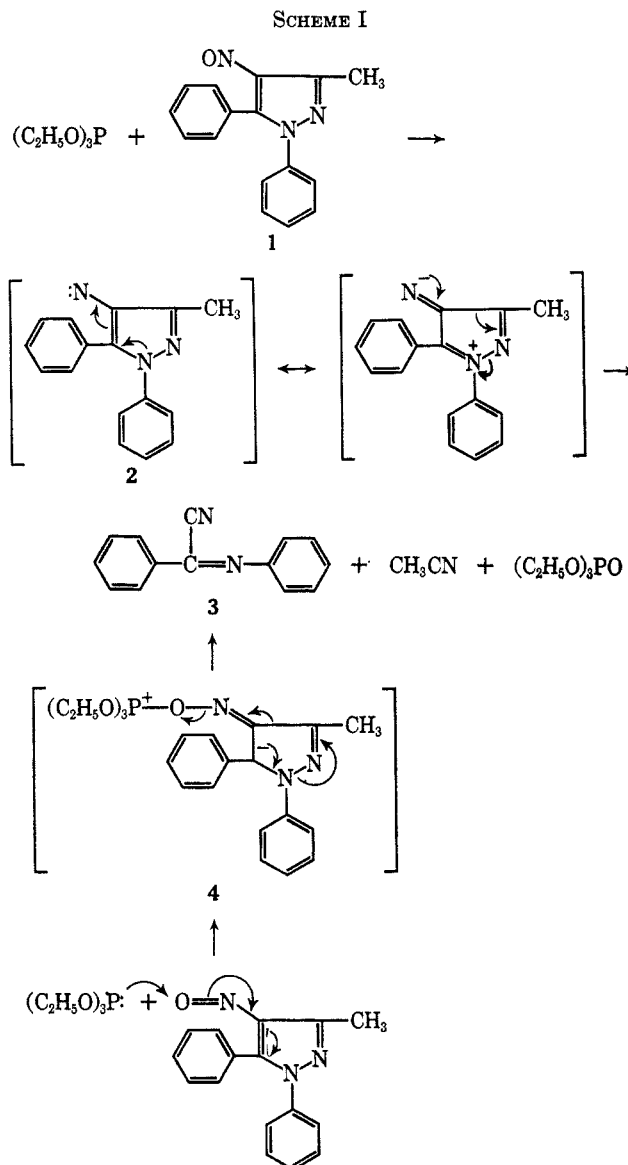
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Bunyan and Cadogan<sup>1,2</sup> have shown that 2-nitrosodiphenyl reacts with triethyl phosphite at 0–5° in

benzene solution to give carbazole in 78% yield. It was postulated that an intermediate nitrene may be involved.<sup>2,3</sup> We were interested in investigating the readily available 1,5-diphenyl-3-methyl-4-nitrosopyrazole<sup>4</sup> (1) in this reaction. The nitrene intermediate from 1 might lead to an indolo[2,3-*d*]pyrazole, but alternatively, the singlet nitrene might be expected also to attract electrons from the pyrazole ring.



When 1,5-diphenyl-3-methyl-4-nitrosopyrazole (1) was treated with triethyl phosphite in benzene solution at 0–5°, according to the general method of Bunyan and Cadogan,<sup>2</sup> no apparent reaction took place. However, when the mixture was heated under reflux, a yellow solid,  $C_{14}H_{10}N_2$ , was isolated. The ir spectrum

(1) P. J. Bunyan and J. I. G. Cadogan, *Proc. Chem. Soc.*, 78 (1962).

(2) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

(3) J. I. G. Cadogan, *Quart. Rev. (London)*, **22**, 222 (1968).

(4) C. N. O'Callaghan and D. Twomey, *Proc. Roy. Irish Acad. Sect. B.*, **64** (13), 187 (1965); *Chem. Abstr.*, **65**, 12191d (1966).