tion was not obtained until the epoxide signals in **5** were shifted to δ 15.

Registry No.—**1**, 2984-50-1; **2**, 286-20-4; **5**, 1464-53-5; **6**, 2426-07-5; **9**, 34905-87-8; **10a**, 34905-88-9; **10b**, 34905-89-0; Eu(DPM)$_3$, 15522-71-1.

Photolysis of 2,6-Di-*tert*-butyl-4-alkylphenols with Polyhalomethanes

RICHARD H. S. WANG

Research Laboratories, Tennessee Eastman Company,
Division of Eastman Kodak Company,
Kingsport, Tennessee 37662

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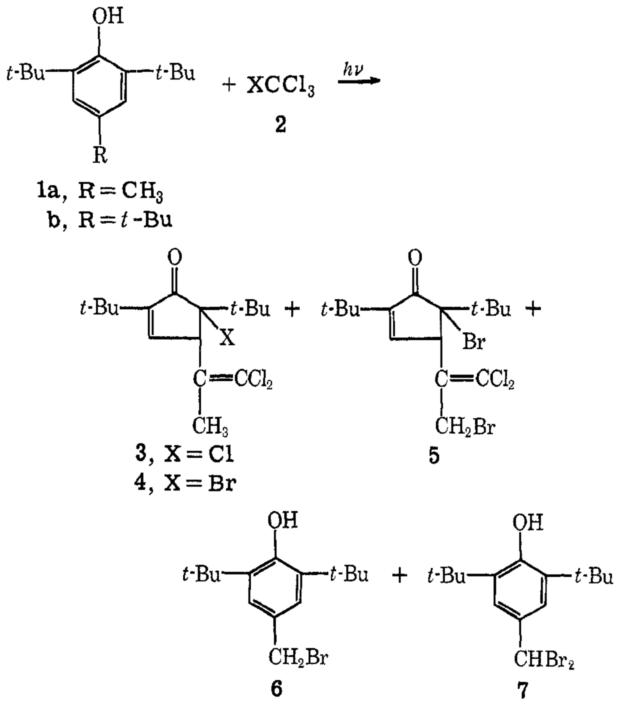
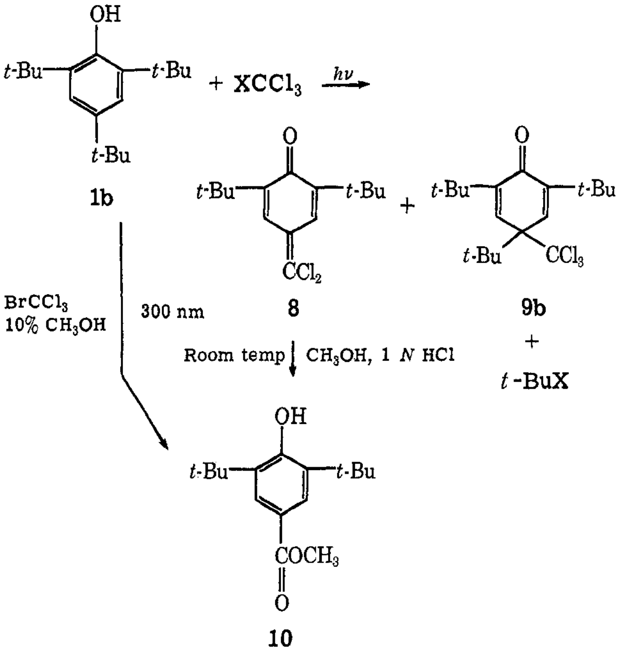
In recent years, a number of studies on photochemical reactions of sterically hindered phenols with various solvents have been published.[1] However, as yet there is little information on the photoreactions of such phenols with polyhalomethanes.

When solutions of 2,6-di-*tert*-butyl-*p*-cresol (**1a**) or 2,4,6-tri-*tert*-butylphenol (**1b**) in either carbon tetrachloride or bromotrichloromethane were irradiated with near-ultraviolet light, two types of photoproducts involving the addition of either a halogen atom or a trichloromethyl radical to the phenol were obtained. The product mixture obtained depended on the structure of the phenol, the solvent used, and, for **1a**, the wavelength of the light used.

The cyclopentenone **3** was the major product of the photolysis of **1a** in carbon tetrachloride when either 300- or 350-nm light was used. When irradiated with 300-nm light in bromotrichloromethane, **1a** gave about 65 mol % of the cyclopentenones **4** and **5** along with 20 mol % of the α-brominated phenol **7**, but, when irradiated with 350-nm light, **1a** gave more of the α-brominated phenols **6** and **7** (40% total) than the cyclopentenone **4** (25%).



The photolysis of **1b** in either carbon tetrachloride or bromotrichloromethane gave the cyclohexadienones **8** and **9b** as well as a *tert*-butyl halide. The same products were obtained whether 300- or 350-nm light was used, but the use of 350-nm light resulted in a much lower conversion of **1b**. Moreover, **10** was produced either by irradiating **1b** in bromotrichloromethane containing 10% methanol or by stirring a mixture of **8** in methanol containing 1 *N* HCl at room temperature for 1 hr.



The thermal reaction of **1a** or **1b** with bromotrichloromethane at 160° in the dark gave only a low yield of chloroform and black tar. Neither 2,2′-azobis(2-methylpropionitrile) (AIBN) nor benzoyl peroxide increased the rate of reaction of **1a** or **1b** with bromotrichloromethane at 80° in the dark. These results, taken with the abilities of **1** and **2** to absorb light at 300 and 350 nm,[2] probably indicate that the excitation of phenol[3] and the rate of generation of a halogen atom and a trichloromethyl radical are the vital factors in the photochemical reactions of **1** with a halotrichloromethane. Therefore, a short-chain or nonchain radical mechanism, as shown in Scheme I, probably accounts for the first stage of these photolyses.

Since carbon tetrachloride does not absorb light in the 350-nm region, the photolyses of **1a** and **1b** in carbon tetrachloride were probably initiated by the excitation of phenol followed by an energy transfer to the carbon tetrachloride, which decomposed to give a chlorine atom and a trichloromethyl radical. These fragments subsequently reacted with phenol to form products. The mechanism shown in Scheme I is consistent with the relative rates of disappearance of **1a** and **1b**; **1a**, which

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[1] (a) H. D. Becker, *J. Org. Chem.*, **32**, 2115 (1967); (b) T. H. Matsuura, Y. Hiromoto, A. Okada, and K. Ogura, *Tetrahedron Lett.*, 3727 (1970).

[2] The optical densities of **1** (0.335 *M* in CH$_2$Cl$_2$) and XCCl$_3$ in a quartz tube (i.d. 1.3 cm) are at 300 nm **1a** = 126, **1b** = 1.3, BrCCl$_3$ = 52, CCl$_4$ = 0.007; at 350 nm, **1a** = 3.0, **1b** = 1.1, BrCCl$_3$ = 0.7, CCl$_4$ = 0. The spectral distribution of an RPR 350-nm lamp ranges from 307 to 420 nm with the maximum emission at 350 nm.

[3] K. Omura and T. Matsuura, *Tetrahedron*, **26**, 255 (1970).

Table I

Photolysis of 2,6-Di-*tert*-butyl-*p*-cresol (1a)

Solvent	λ, nm	Phenol reacted, %	Products, %[a] 3[b]	4[b]	5[b]	6[b]	7[b,c]	$CHCl_3$[d]	*t*-BuBr[d]	*t*-BuCl[d]
$BrCCl_3$	300	90		30	35		20	45		
	350	80		25		30	10	60		
CCl_4	300	60	35					4		
	350	10	10							

[a] Based on the amount of phenol added. [b] Measured by nmr spectra. [c] Based on the amount of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, hydrolysis product of 7. [d] Measured by glpc.

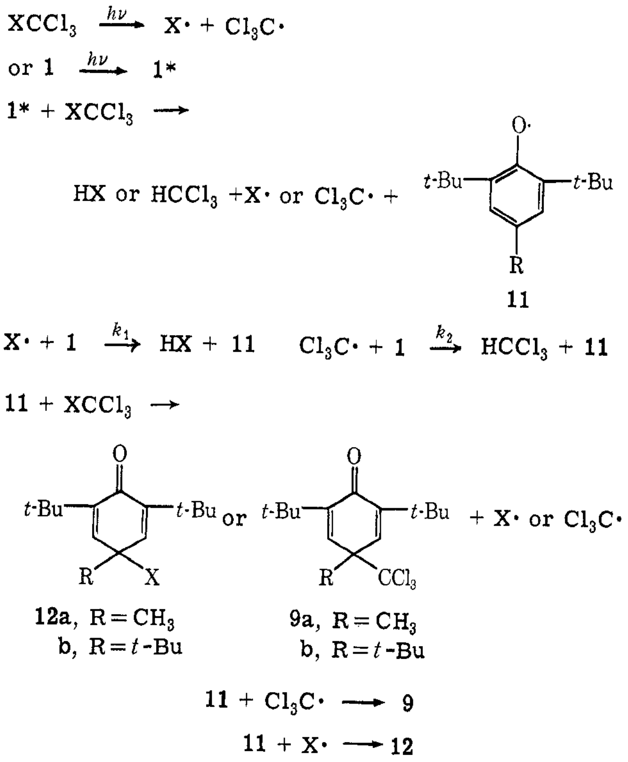
Table II

Photolysis of 2,4,6-Tri-*tert*-butylphenol (1b)

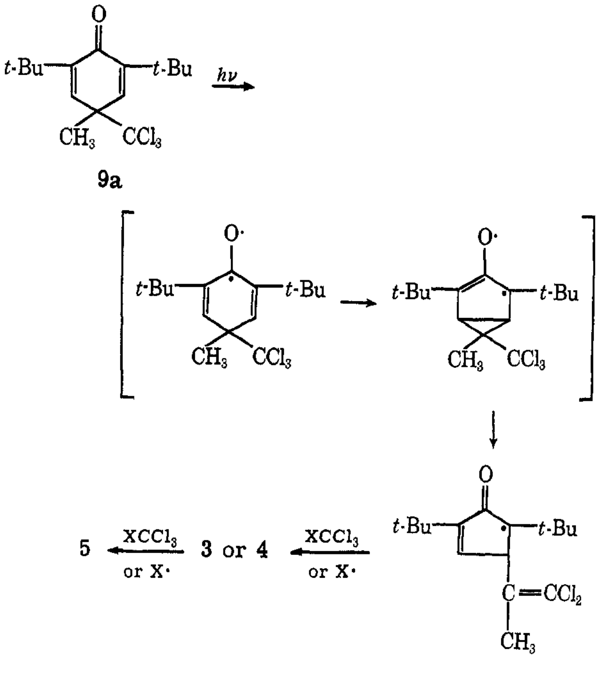
Solvent	λ, nm	Phenol reacted, %	Products, %[a] 8[b]	9[b]	$CHCl_3$[c]	*t*-BuBr[c]	*t*-BuCl[c]
$BrCCl_3$	300	70	35	8	27	26	15
	350	5	trace	3	<1	11	11
CCl_4	300	40	10	25	5		10
	350	2	trace	trace	<1		1

[a] Based on the amount of phenol added. [b] Measured by nmr spectra. [c] Measured by glpc.

Scheme I



Scheme II



absorbs much more strongly at 350 nm than 1b, reacted about five times faster with carbon tetrachloride than did 1b (Tables I and II).

The order of hydrogen atom abstraction from hydrocarbons by the radical species involved in the reactions of Scheme I is known to be Cl· > Cl_3C· ≥ Br·;[4,5] hence, in carbon tetrachloride $k_1 > k_2$, and a little chloroform was formed. Both 1a and 1b would give a cyclohexadienone intermediate, 9a and 9b. The courses of the subsequent reactions depend on the nature of R. When R = CH_3 (9a), photorearrangement[6] of 9a would give 3 or 4 and allylic bromination of 4 would give 5 (Scheme II).

Because the *tert*-butyl group can be cleaved from an aromatic ring,[7] 9b reacts further by a path different from that for 9a. It reacts probably *via* expulsion of a *tert*-butyl radical to form a phenoxy radical 13 and subsequently to produce 8 (Scheme III).[8]

Neither 12a nor 12b was detected in any of the reaction mixtures, probably because both were photounstable. When 1a was irradiated in bromotrichloromethane, 12a, formed along with 9a, rearranged[9] immediately to form the α-brominated phenols 6 and 7 (Scheme IV).

The structures of various photolytic products were deduced from spectroscopic measurements and elemental analyses. The maximum uv absorptions of compounds 3, 4, and 5 at 235, 236, and 237 nm, respectively,

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(4) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 48–50.

(5) J. M. Tedder, *Quart. Rev., Chem. Soc.*, **14**, 344 (1960).

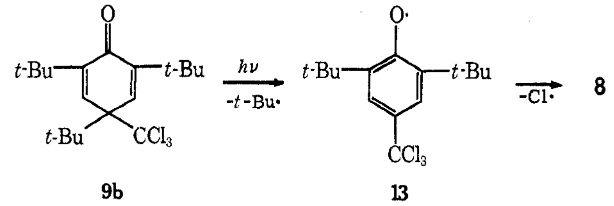
(6) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137 (1968).

(7) T. Matsurra and K. Ogura, *ibid.*, **89**, 3846 (1967).

(8) The acid-catalyzed expulsion of a *tert*-butyl group from **9b** by mixing **9b** with methanol containing 1 *N* HCl at room temperature for 20 hr failed to produce **10**, and only **9b** was recovered.

(9) V. D. Pokhodenko and N. N. Kalibabchu, *Zh. Org. Khim.*, **2**, 1397 (1966).

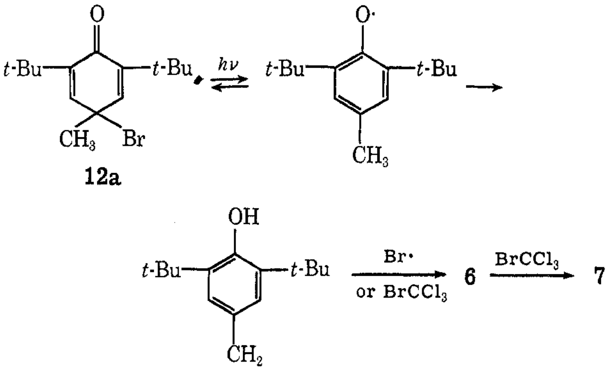
Scheme III



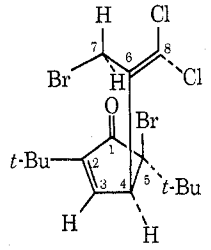
$t\text{-Bu}\cdot + Cl\cdot \longrightarrow t\text{-BuCl}$

$t\text{-Bu}\cdot + BrCCl_3 \text{ (or Br}\cdot) \longrightarrow t\text{-BuBr}$

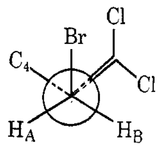
Scheme IV



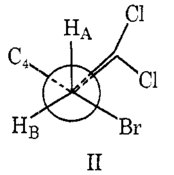
indicate a possible cyclopentenone structure.[10] In the infrared, **3** and **4** have nearly identical spectra with two major bands at 1710 and 1625 cm^{-1} (cyclopentenone carbonyl group and a dichloro-substituted double bond[6]). The nmr spectra (see Experimental Section) of **3** and **4** are also consistent with the assignment of the cyclopentenone structures. The infrared spectrum of **5** is not identical with the spectra of **3** or **4**, but it also shows strong bands at 1710 and 1630 cm^{-1}. However, the nmr spectrum of **5** gives three signals distinctively different from those of **3** and **4**. After investigations of the splittings and the coupling constants of those signals, it was concluded that **5** actually has a cyclopentenone structure similar to the cyclopentenone structures of **3** and **4**. The chemical shifts of δ 1.15 (9 H, s), 1.30 (9 H, s), and 4.35 (1 H, d, J = 3.0 Hz), which are similar to those of **3** and **4**, were assigned to the two *tert*-butyl groups at C_2 and C_5 and to the tertiary hydrogen at C_4, respectively. The two protons at C_7 are nonequivalent in the three rotomers (I–III); hence, the chemical shifts of δ 3.35 (1 H, J = 11.0 Hz) and 4.25 (1 H, J = 11.0 Hz) can reasonably be assigned to the methylene protons at C_7. The proton at δ 7.30 (1 H, J = 3.0 Hz) is believed to be adjacent to the proton at C_4; hence, it must be the vinyl proton at C_3 in structure A. Although the bromine atom at C_7 would not be expected to directly affect the chemical shift of the vinyl proton at C_3 through the σ bonds, the steric restriction in A would allow the bromine atom to be close enough to affect the vinyl proton at C_3 inductively through space; hence, the chemical shift of the vinyl proton at C_3 appears at a lower field (δ 7.30) in **5** than in **3** and **4**.



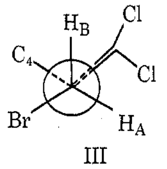
A



I



II



III

The structures of **8** and **9** are fully supported by their spectroscopic data and elemental analyses (see Experimental Section).

Experimental Section[11]

The photolytic reactions were carried out in a Rayonet reactor, Model RPR-100. The RPR 300- and 350-nm lamps were used as light sources without filters. All melting points are uncorrected and were measured with a Thomas-Hoover capillary melting point apparatus. The ultraviolet spectra were recorded on a Cary 14 spectrophotometer. The nmr spectra were determined with a Varian A-60 spectrophotometer with tetramethylsilane as an internal standard. The mass spectra were recorded on a Consolidated Electrodynamic 21-110B mass spectrometer.

General Photolysis Procedure.—A solution of 5 mmol of the desired phenol in 15 ml of polyhalomethane, contained in a quartz tube (i.d. 1.30 cm), was flushed with nitrogen for 5 min and then irradiated with either 300- or 350-nm light for 20 hr. A 1-ml aliquot was analyzed by glpc to determine the amount of volatile products, such as chloroform and *tert*-butyl halides, present. The solvent was removed, and the remainder was analyzed by nmr spectroscopy to determine the molar proportions of various products (Tables I and II).

2,5-Di-*tert*-butyl-5-chloro-4-(2,2-dichloro-1-methylvinyl)-2-cyclopenten-1-one (3).—After the irradiation of **1a** in carbon tetrachloride with 300-nm light, the solvent was removed from the reaction mixture, and the residue was dissolved in absolute ethanol. **3** was obtained after three recrystallizations from ethanol (0.42 g, 42%, white needles): mp 99–101°; ir (KBr) 1710 (cyclopentenone carbonyl group) and 1625 cm^{-1} (C=CCl$_2$); uv max (CH$_2$Cl$_2$) 235 nm (log ϵ 3.99); mass spectrum m/e 336 (M$^+$ with three chlorines); nmr (CDCl$_3$) δ 1.10 (9 H, s, *t*-Bu), 1.20 (9 H, s, *t*-Bu), 1.60 (3 H, s, CH$_3$), 4.30 (1 H, d, J = 3.0 Hz, *t*-H), and 6.85 (1 H, d, J = 3.0 Hz, vinyl proton).

Anal. Calcd for $C_{16}H_{23}Cl_3O$ (337.38): C, 56.91; H, 6.82; Cl, 31.53. Found: C, 57.00; H, 6.82; Cl, 31.25.

5-Bromo-2,5-di-*tert*-butyl-4-(2,2-dichloro-1-methylvinyl)-2-cyclopenten-1-one (4).—After the irradiation of **1a** in bromotrichloromethane with 350-nm light, the solvent was removed from the reaction mixture, and the residue was recrystallized three times from ethanol to give **4** as white needles (0.35 g, 23%): mp 126–128°; ir (KBr) 1710 (cyclopentenone carbonyl group) and 1625 cm^{-1} (C=CCl$_2$); uv max (CH$_2$Cl$_2$) 236 nm (log ϵ 3.95); nmr (CDCl$_3$) δ 1.10 (9, H, s, *t*-Bu), 1.20 (9 H, s, *t*-Bu), 1.60 (3 H, s, CH$_3$), 4.25 (1 H, d, J = 3.0 Hz, *t*-H), and 6.85 (1 H, d, J = 3.0 Hz, vinyl proton).

Anal. Calcd for $C_{16}H_{23}BrCl_2O$ (381.73): C, 50.28; H, 6.02; Br, 20.93; Cl, 18.57. Found: C, 49.95; H, 5.99; Br, 21.01; Cl, 18.72.

The residue which remained after evaporation of the combined filtrates from the recrystallizations of **4** was dissolved in 10 ml of petroleum ether (bp 30–60°) and eluted through a silica gel column (0.05–0.20 mm, 35.0 × 2.5 cm) with additional petroleum ether. The first 50-ml portion of eluate contained mostly **1a**. The second 50-ml portion contained about equal amounts of **1a** and **α-bromo-2,6-di-*tert*-butyl-*p*-cresol (6)**; the presence of **6** was shown by nmr analysis [δ 4.30 (2 H, CH$_2$Br) and 7.01 (2 H,

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[10] R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *J. Amer. Chem. Soc.*, **70**, 1379 (1948).

[11] The actual yields of various products are based on the actual amount of **1** reacted.

aromatic)], which was consistent with the nmr analysis of an authentic sample of **6**.[12]

5-Bromo-2,5-di-*tert*-butyl-4-[1-(bromomethyl)-2,2-dichlorovinyl]-2-cyclopenten-1-one (5).—After the irradiation of **1a** in bromotrichloromethane with 300-nm light, the solvent was removed from the reaction mixture, and the residue was recrystallized five times from absolute ethanol to give **5** (0.28 g, 13.5%) as white needles: mp 180–182°; ir (KBr) 1710 (cyclopentenone carbonyl group) and 1630 cm^{-1} (C=CCl$_2$); uv max (CH$_2$Cl$_2$) 237 nm (log ε 4.18); mass spectrum *m/e* 460 (M$^+$ with two bromines and two chlorines); nmr (CDCl$_3$) δ 1.15 (9 H, s, *t*-Bu), 1.30 (9 H, s, *t*-Bu), 4.35 (1 H, d, J = 3.0 Hz, *t*-H), 7.30 (1 H, d, J = 3.0 Hz, vinyl proton), and 3.35 and 4.25 (2 H, 2 d, $J_{HA} = J_{HB}$ = 11.0 Hz, CH$_A$H$_B$Br).

Anal. Calcd for C$_{16}$H$_{22}$Br$_2$Cl$_2$O (460.74): C, 41.67; H, 4.77; Br, 34.69; Cl, 15.39. Found: C, 41.78; H, 4.84; Br, 34.27; Cl, 15.43.

The residue which remained after evaporation of the combined filtrates from the recrystallizations of **5** was dissolved in 10 ml of petroleum ether and eluted through a silica gel column with additional petroleum ether. The first 20 ml of the petroleum ether fraction contained about 0.01 g of low-melting (35–45°) material, shown by its nmr spectrum to be a mixture of 10% of **1a** and about 90% of a second component. The following spectroscopic data are consistent with the assignment of the **2,5-di-*tert*-butyl-4-methyl-4-(trichloromethyl)-2,5-cyclohexadien-1-one (9a)** structure to the major component of this mixture: ir (neat) 1650 and 1670 cm^{-1} (double strong bands, cyclohexadienone carbonyl group[13]); nmr (CDCl$_3$) δ 1.25 (18 H, s, 2 *t*-Bu), 6.70 (2 H, s, two vinyl protons), and 1.62 (3 H, s, CH$_3$); mass spectrum *m/e* 336 (M$^+$ with three chlorines), major fragments at *m/e* (rel intensity) 219 (96), 189 (13), 177 (42), 163 (17), 57 (100), and 41 (37); an intense metastable peak was observed at an apparent mass of 143 which results from the transition of M$^+$ (336) → M$_1^+$ (219) + Cl$_3$C$^+$ (117). After the elution of the first 20-ml fraction, an additional 100 ml of petroleum ether was added to the column to remove the rest of **1a** and **12a**. Then 50 ml of methylene chloride was passed through the column. Evaporation of the methylene chloride gave a brown tar which was refluxed in 90% ethanol for 30 min. On cooling, white crystals were formed and were identified as **3,5-di-*tert*-butyl-4-hydroxybenzaldehyde** (0.11 g, 10.5%), mp 188–189° (lit.[14] mp 189°). The aldehyde was assumed to result from the hydrolysis of **7** with 90% ethanol.[15] The column was again eluted, this time with 50 ml of methanol, and 0.15 g (8.8%) of **4** was isolated.

2,6-Di-*tert*-butyl-4-(dichloromethylene)-2,5-cyclohexadien-1-one (8).—After the irradiation of **1b** in bromotrichloromethane with 300-nm light, the solvent was removed from the reaction mixture, and the residue was recrystallized five times from absolute ethanol to give **8** as light yellow leaflet crystals (0.30 g, 30%): mp 91–93°; ir (KBr) 1630 (C=O) and 1590 cm^{-1} (conjugated C=CCl$_2$); uv max (CH$_2$Cl$_2$) 323 nm (log ε 4.15); nmr (CDCl$_3$) δ 1.40 (18 H, s, 2 *t*-Bu) and 7.30 (2 H, s, two vinyl protons); mass spectrum *m/e* 286 (M$^+$ with two chlorines).

Anal. Calcd for C$_{15}$H$_{20}$Cl$_2$O (286.91): C, 62.74; H, 6.97; Cl, 24.72. Found: C, 62.59; H, 6.92; Cl, 24.58.

A mixture of **8** in methanol containing 1 *N* HCl was stirred at room temperature for 1 hr. The white precipitate formed was identified as **methyl(3,5-di-*tert*-butyl-4-hydroxy)benzoate (10)**, mp 156–158° (lit.[16] mp 159°).

2,4,6-Tri-*tert*-butyl-4-(trichloromethyl)-2,5-cyclohexadien-1-one (9b).—After the irradiation of **1b** in carbon tetrachloride with 300-nm light, the solvent was removed from the reaction mixture, and the residue was recrystallized three times from absolute ethanol to give **9b** as white needles (0.32 g, 56%): mp 69–71; ir (KBr) 1660 and 1640 cm^{-1} (double strong bands, carbonyl group of cyclohexadienone[13]); uv max (CH$_2$Cl$_2$) 248 nm (log ε 3.95) and 322 (3.87); nmr (CDCl$_3$) δ 1.24 (9 H, s, *t*-Bu), 1.26 (18 H, s, 2 *t*-Bu), and 6.95 (2 H, s, two vinyl protons).

Anal. Calcd for C$_{19}$H$_{29}$Cl$_3$O (379.38): C, 60.10; H, 7.64; Cl, 28.04. Found: C, 59.95; H, 7.65; Cl, 27.97.

Attempted Thermal Reaction of 2,6-Di-*tert*-butyl-4-alkylphenol with Bromotrichloromethane.—A mixture of 5 mmol of **1a** or **1b** and 15 ml of bromotrichloromethane was sealed in a Pyrex tube and heated at 160°. After 10 hr, the solution was dark brown, but no product, other than some chloroform which was identified by glpc, could be isolated. When a similar mixture was heated at 80° in the presence of either AIBN or benzoyl peroxide, no reaction occurred, even after 2 days.

Registry No.—**1a**, 128-37-0; **1b**, 732-26-3; **3**, 34982-09-7; **4**, 34957-03-4; **5**, 34959-60-9; **8**, 34959-61-0; **9a**, 34959-62-1; **9b**, 34959-63-2.

Acknowledgment.—The author thanks Dr. G. R. Lappin for encouragement and for discussions of this work and is grateful to Mr. H. D. Kinder and Mr. J. C. Gilland for spectroscopic analyses.

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[12] T. Fujisaki and T. Miyazaki, *Chem. Abstr.*, **35**, 11345*b* (1963).

[13] W. H. Pirkle and G. F. Koser, *J. Amer. Chem. Soc.*, **90**, 3598 (1968).

[14] T. W. Campbell and G. M. Coppinger, *ibid.*, **74**, 1469 (1952).

[15] L. K. Popov, F. M. Egidis, and V. V. Ershov, *Bull. Acad. Sci. USSR*, **4**, 863 (1968).

[16] A. Hausweiler, R. Seydel, and R. Stroh, *Chem. Abstr.*, **55**, 27217*h* (1961).

The Chemistry of Flavandiones. Reaction with Diazomethane[1a]

M. A. Smith,* W. D. Boswell, Jr.,[1b]
K. G. Henzel, and D. G. Miller

Department of Chemistry, Bucknell University,
Lewisburg, Pennsylvania 17837

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Flavonols **1** are oxidized by periodic acid, 1 mol of oxidant being consumed.[2,3] When methanol is the solvent, the products are the methyl 3-hemiketals of 2-methoxy-3,4-flavandiones **2**.[4] Solutions of these hemiketals are an equilibrium mixture of **2** and the free dione, this being responsible for the solutions' yellow color.

When the hemiketals **2a–d** are mixed with an ethereal solution of diazomethane, they are converted to the epoxides **3**. This formulation is supported by elemental analysis, spectra, and chemical reactivity.

Before the advent of routine ir and nmr spectra, α-diketones were generally believed to form 1,3-dioxoles with diazomethane.[5] Later work by Eistert[6] established that these products were generally epoxides, although exceptions are known.[7] However, the products from diazomethane and **2a–d** all have strong bands in the carbonyl region and this renders a dioxole structure most unlikely.

With monoketones and diazomethane, epoxide formation competes with methylene insertion. This has been observed with α-diketones also. Diazomethane in ether converts phenanthraquinone into an epoxide, but, in the presence of much methanol, a ring-expanded product is found.[8] However, the spectral properties of the diazomethane products from **2a–d** are hardly consistent with those expected for any ring-expanded product. In our case, such a product could be either of a pair of α-diketones or a β-diketone. In the ketone form, any of these diketones would have two bands in

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[1] (a) Supported in part by the National Institute of General Medical Sciences, National Institutes of Health, U. S. Public Service (Grant No. 11830). (b) National Science Foundation Undergraduate Research Participant, summer, 1966.

[2] M. A. Smith and B. R. Willeford, *Anal. Chem.*, **26**, 751 (1954).

[3] M. A. Smith, *J. Org. Chem.*, **28**, 933 (1963).

[4] M. A. Smith, R. A. Webb, and L. Cline, *ibid.*, **30**, 995 (1965).

[5] C. D. Gutsche, *Org. React.*, **8**, 364 (1954).

[6] B. Eistert, G. Fink, and R. Wollheim, *Chem. Ber.*, **91**, 2710 (1958).

[7] B. Eistert and L. Klein, *ibid.*, **101**, 391 (1968).

[8] B. Eistert, R. Wollheim, G. Fink, and H. Minas, and L. Klein, *ibid.*, **101**, 84 (1968).