Thermal, Photochemical, and Photonucleated Thermal Dehydration of *p*-Hydroxytriarylmethanols in the Solid State. (3,5-Dimethyl-4-hydroxyphenyl)diphenylmethanol and (3,5-Dibromo-4-hydroxyphenyl)diphenylmethanol. X-ray Crystal Structures of (4-Hydroxyphenyl)diphenylmethanol and Its 3,5-Dimethyl Derivative[1,2]

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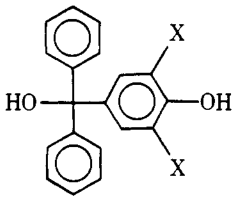
Abstract: (4-Hydroxyphenyl)diphenylmethanol (**1a**), (3,5-dibromo-4-hydroxyphenyl)diphenylmethanol (**1b**), and (3,5-dimethyl-4-hydroxyphenyl)diphenylmethanol (**1c**) have been found to constitute a class of compounds which crystallizes with the phenolic hydroxyl prealigned by hydrogen bonding to an alcoholic hydroxyl group of an adjacent molecule in a fashion suitable for a self-catalyzed dehydration reaction to form the corresponding yellow or orange fuchsones (**2a**, **2b**, and **2c**). The solid-state thermal reactions of these compounds previously observed by Gomberg and his associates have been extended to observations of single crystals and some preference for reaction in the direction of the hydrogen-bonded chains noted. The photochemical reaction which had been observed by Gomberg has been extended to single crystals and, most interesting, it has been found possible to photonucleate the thermal reactions of **1b** and **1c**. The crystal structures of **1a** and **1c** have been determined by X-ray methods. Colorless crystals of **1a** are monoclinic, a = 8.816 (3) Å, b = 15.379 (4) Å, c = 10.863 (4) Å, β = 101.43 (3)°; the space group is $P2_1/c$ and the structure has been refined to an R factor of 0.061 on 2265 nonzero reflections. The hydroxylic protons were found to be disordered. Colorless crystals of **1c** are monoclinic, a = 22.394 (5) Å, b = 8.580 (3) Å, c = 17.556 (7) Å, β = 99.20 (2)°; the space group is $C2/c$. **1c** is isostructural with **1b** whose structure was previously determined. Molecules of **1c** are linked by hydrogen bonds between the phenolic and alcoholic hydroxyl groups but there are in addition hydrogen bond cross-links. The time for 90% dehydration of the crystalline dibromophenol **1b** at 110 °C was approximately one-tenth the value for the isostructural dimethyl compound **1c**.

Introduction

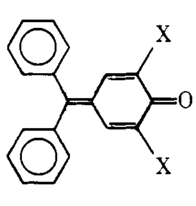
A major focus of interest in solid-state organic chemistry[3] is on the utilization of the crystalline state to lock molecules into orientations favoring a desired reaction. Examples have included conformational locking of substrate molecules to favor a stereospecific elimination produced by a gaseous reagent.[4] A second approach involves the juxtaposition of two or more reactant molecules with reactive positions correctly aligned for the intermolecular reaction desired. This second class of examples includes photochemical [2 + 2] cycloadditions[5] and nucleophilic displacement reactions.[6] A reaction from this latter class and which has been investigated in our laboratory is an acid–base-catalyzed dehydration of a carbinolhydrazine to a hydrazone.[7] In this case, the acid and base are approximately prealigned by hydrogen bonding in the crystal before reaction.

In a search for further examples of the latter sort we were attracted to the thermal dehydration of certain *p*-hydroxytriarylmethanols (**1**)[8,9] which seemed to possess a combination of functional groups which should lead to a general molecular packing characterized by hydrogen bonding of the relatively good hydrogen-donating phenolic hydroxyl group directed toward the relatively good hydrogen-accepting alcoholic hydroxyl group of an adjacent molecule.[10] In fact, the crystal structure of the dibromo derivative **1b** had been reported.[9] Although the determination of structure **1b** was not of sufficient precision to locate the hydroxylic protons, it suggested that the hydrogen-bonding pattern was that desired for promotion of the dehydration reaction.

In this paper we describe the synthesis of the dimethyl analogue **1c**, the determination of the crystal structures of **1a** and **1c**, and the thermal, photochemical, and photolytically induced thermal reactions of **1b** and **1c**.



1a, X = H
b, X = Br
c, X = CH_3



2a, X = H
b, X = Br
c, X = CH_3

Experimental Section

Spectra and other supplementary experimental data are available in ref 1a.

Synthesis and Characterization of Compounds. (3,5-Dimethyl-4-hydroxyphenyl)diphenylmethanol (1c). Stirring the fuchsone **2c** in a Me_2SO-H_2O-NaOH solution under N_2 overnight, followed by filtration, dilution with H_2O, and precipitation of the carbinol with CO_2 gas,[11] gave yellowish product (90% yield). Recrystallization from toluene gave **1c** as a white powder: mp 188–189 °C, turning yellow ~150 °C; IR (KBr pellet) 3400, 1495, 1485, 1450, 1205, 1180, 1100, 700 cm^{-1}; NMR (Me_2SO-d_6) 8.00 (1 H, s), 7.18 (10 H, s), 6.69 (2 H, s), 6.02 (1 H, s), 2.07 ppm (6 H, s), the signals at 8.00 and 6.02 ppm diminished on dilution with D_2O; UV λ_{max}, nm ($\epsilon \times 10^{-3}$) 277 (1.59), 284 (1.59); DSC, sharp endotherm, extrapolated onset 200 °C, broad endotherm centered at 270 °C.

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.63. Found: C, 83.00; H, 6.86.

Crystals from ether–benzene (habit I) were rectangular tablets elongated along [001] with {100} as the most prominent faces and displayed 2/*m* symmetry: interfacial angles (deg), ±1° (calcd) (100), $(00\bar{1})$ 100 (99); (100), (110) 69 (69); $(\bar{1}00)$, (001) 82 (81); $(00\bar{1})$, (110) 94 (93); (001), (110) 87 (87); $(1\bar{1}0)$, (110) 138 (138).

Crystals from ether–hexane (habit II) were six-sided tablets with {001} as the prominent faces and displayed 2/*m* symmetry: interfacial

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angles (deg), ±1° (calcd) (001), (100) 81 (81); (001), (110) 87 (87); $(1\bar{1}0)$, (100) 68 (69); $(1\bar{1}0)$, (110) 137 (138); $(1\bar{1}0)$, $(\bar{1}10)$ 179 (180); (110), $(\bar{1}10)$ 42 (42); (110), $(\bar{1}00)$ 112 (111); (100), $(\bar{1}10)$ 111 (111).

2,6-Dimethyl-4-(*α*,*α*-diphenylmethylene)-1,4-benzoquinone (2c). The method of Gomberg and Jickling[12] was adapted to **2c**. From 20 g (0.16 mol) of 2,6-dimethylphenol and 17.4 g (0.07 mol) of dichlorodiphenylmethane was obtained 15 g (75% yield) of the fuchsone **2c**. Recrystallization from hexane-benzene gave **2c** as a yellow-orange powder: mp 200-202 °C (lit.[13] mp 201-202 °C); IR (KBr pellet) 1630, 1600, 1510, 1030, 700 cm^{-1}; NMR (CD_2Cl_2) 7.13-7.47 (12 H, m), 1.97 ppm (6 H, s); UV λ_{max}, nm ($\epsilon \times 10^{-4}$) 262 (1.53), 365 (3.07).

(3,5-Dibromo-4-hydroxyphenyl)diphenylmethanol (1b). The reaction of methyl 3,5-dibromo-4-hydroxybenzoate[14] with phenylmagnesium bromide gave, after recrystallization from ether-hexane, a white powder: mp 137-139 °C (turning yellow ~120-125 °C) (lit.[15] mp 138 °C); IR (KBr pellet) 3450, 1475, 1450, 1160, 700 cm^{-1}; NMR (acetone-d_6) 8.43 (1 H, s), 7.39 (2 H, s), 7.30 (10 H, s), 5.41 ppm (1 H, s), the signals at 8.43 and 5.41 ppm diminished on dilution with D_2O; UV λ_{max}, nm ($\epsilon \times 10^{-3}$) 285 (2.20), 293 (2.68); DSC, sharp endotherm, extrapolated onset 140 °C, broad ill-defined endotherm centered ~210 °C, sharp endotherm, extrapolated onset ~238 °C.

Crystals from ether–hexane were six-sided tablets with {001} as the prominent faces and displayed 2/*m* symmetry: interfacial angles (deg), ±1 (calcd) (001), (100) 81 (80); (001), $(\bar{1}\bar{1}0)$ 94 (94); $(1\bar{1}0)$, (100) 68 (68); $(1\bar{1}0)$, (110) 136 (137); $(1\bar{1}0)$, $(\bar{1}\bar{1}0)$ 44 (43); $(\bar{1}10)$, $(\bar{1}00)$ 70 (68); (100), $(\bar{1}00)$ 180 (180); (110), $(\bar{1}00)$ 112 (112). Crystals corresponding to habit I of **1c** were not observed.

2,6-Dibromo-4-(*α*,*α*-diphenylmethylene)-1,4-benzoquinone (2b) was prepared in virtually quantitative yield by the thermal dehydration of a powdered sample of **1b** at 110 °C for 30 h. Recrystallization from hexane–benzene gave reddish-orange crystals: mp 236–238 °C (lit.[15] mp 238 °C); IR (KBr pellet) 1640, 1590, 1505, 1310, 700 cm^{-1}; NMR ($CDCl_3$) 7.80 (2 H, s), 7.20-7.75 ppm (10 H, m); UV λ_{max}, nm ($\epsilon \times 10^{-4}$) 276 (1.53), 396 (2.84).

(*p*-Hydroxyphenyl)diphenylmethanol (1a) was prepared by the method of Gomberg and Jickling[12] and separated from undesired side products by column chromatography on silica gel (ether-hexane eluant) or by the reaction of ethyl *p*-hydroxybenzoate with phenylmagnesium bromide in somewhat better yields. Repeated recrystallization from EtOH-H_2O plus 1 drop of NH_4OH followed by repeated recrystallization from toluene-heptane at −80 °C gave **1a** as a white powder: mp 157-159 °C, turning yellow ~110-120 °C (lit.[16] mp 157-159 °C); UV λ_{max}, nm ($\epsilon \times 10^{-3}$) 280 (1.75), 286 (1.39); DSC, broad endotherm centered at 117 °C, sharp endotherm, extrapolated onset 170 °C.

When **1a** was recrystallized from dilute EtOH-AcOH or from 50% AcOH, there was obtained a yellow powder, mp 139-140 °C (lit.[17] mp 139-140 °C), determined from the UV spectra of pure **1a** (white) and **2a** to be composed of ~99% **1a** and ~1% **2a** in agreement with results reported earlier.[8] The IR, NMR, and elemental analyses of both the white and yellow powders of **1a** were effectively identical; IR (KBr pellet) 3500, 1600, 1375, 1285, 1180, 1157, 700 cm^{-1}; NMR (acetone-d_6) 8.18 (1 H, s), 7.22 (10 H, broad s), distorted AB quartet, A 7.04, B 6.70, $J_{AB} = 9$ Hz (4 H), 4.93 ppm (1 H, s), the signals at 8.18 and 4.93 ppm diminished on dilution with D_2O.

Crystals from ether–benzene were cube shaped with {120} and {001} as the prominent faces and showed 2/*m* symmetry: interfacial angles (deg), ±1° (calcd) (001), (120) 83 (82); (001), $(\bar{1}20)$ 97 (98); (120), $(1\bar{2}0)$ 98 (97); (120), $(\bar{1}20)$ 83 (83); (120), $(\bar{1}\bar{2}0)$ 180 (180); $(\bar{1}20)$, $(\bar{1}20)$ 179 (180).

Although crystals of **1a** suitable for comprehensive solid-state work were not obtained, the thermal reactions of imperfect chips were observed under the microscope at temperatures of 70–100 °C; the yellow coloration due to the formation of **2a** was observed. However, no detailed solid-state work on the rearrangement of crystals of **1a** was carried out. Several attempts (cocrystallization of **1a** and **2a** and heating of a microcrystalline sample of **1a** at 90 °C for varying lengths of time) to obtain the 1:1 complex of **1a**:**2a** reported by Baeyer and Villiger[18] were unsuccessful.

***α*,*α*-Diphenylmethylene-1,4-benzoquinone (2a).** Thermal dehydration of solid **1a** at 110 °C for 24 h followed by recrystallization of the glassy, orange-red residue from cyclohexane and purification by sublimation (100 °C, 0.01 Torr) gave **2a**: mp 166-169 °C (lit.[18] mp 168-170 °C); IR (KBr pellet) 3060, 1620, 1600, 760, 705 cm^{-1}; NMR ($CDCl_3$) 7.08-7.52 (12 H, m), 6.4 ppm (2 H, d, $J = 10$ Hz), half of a distorted AB quartet; UV λ_{max}, nm ($\epsilon \times 10^{-4}$) 260 (1.35), 365 (2.76).

X-ray Structure Determinations. (3,5-Dimethyl-4-hydroxyphenyl)diphenylmethanol (1c). A crystal of **1c** (dimensions 0.4 × 0.4 × 0.2 mm) suitable for X-ray work was obtained by slow evaporation of an ether-benzene solution.

Crystal Data: $C_{21}H_{20}O_2$; mol wt 304.4; monoclinic; $a = 22.394$ (5) Å, $b = 8.580$ (3) Å, $c = 17.556$ (4) Å, $\beta = 99.20$ (2)°; $V = 3330$ Å^3; $Z = 8$; $d_c = 1.21$ g/cm^3; $F(000) = 1296$; systematic absences, *hkl* when $h + k = 2n + 1$, *h*0*l*, when $l = 2n + 1$; space group *C*2/*c* or *Cc*, the former was confirmed by the results of the analysis. Unit cell parameters were determined by a least-squares fit to the settings for 14 accurately centered high-order reflections (Cu K*α*, = 1.541 78 Å).

Intensity data were collected on a computer-controlled four-circle Syntex P2$_1$ diffractometer. Procedures for data collection have been described previously.[19] A total of 2202 reflections was considered nonzero at the 1.96*σ* significance level out of 2837 possible reflections in the 2*θ* range 2-130°. Absorption or extinction corrections were not applied and there was no evidence for crystal decomposition.

The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. The atomic scattering factors were taken from the analytical expressions given in the International Tables for X-ray Crystallography.[20]

The structure was solved using the MULTAN program.[21] Least-squares refinement incorporating positional and anisotropic temperature parameters for the nonhydrogen atoms gave an *R* factor of 0.091. The positions of the aromatic hydrogen atoms were obtained by applying standard geometric criteria; those for the hydrogen atoms of the methyl groups and for the hydroxyl hydrogen atoms were obtained from difference maps. The final model was obtained by full-matrix least-squares refinement varying positional and anisotropic temperature parameters for all nonhydrogen atoms and positional and isotropic temperature parameters for all hydrogen atoms to convergence with a final *R* factor of 0.056 and an R_2 of 0.063.[22] The "goodness of fit" between the calculated and observed models was 2.06.[22] A final difference map did not reveal any significant electron density above 0.19 e/Å^3.

The final atomic coordinates for **1c** are listed in Table I. The final values of the thermal parameters and of the structure factors have been deposited.[23]

(*p*-Hydroxyphenyl)diphenylmethanol (1a). A crystal of **1a** (dimensions 0.3 × 0.3 × 0.1 mm) suitable for X-ray analyses was obtained by slow evaporation of an ether-hexane solution.

Crystal Data: $C_{19}H_{16}O$; mol wt 276.1; monoclinic; $a = 8.816$ (3) Å, $b = 15.379$ (4) Å, $c = 10.863$ (4) Å, $\beta = 101.43$ (3)°; $V = 1444$ Å^3; $Z = 4$; $d_c = 1.27$ g/cm^3; $F(000) = 584$; systematic absences, *h*0*l* when $l = 2n + 1$, 0*k*0 when $k = 2n + 1$; space group $P2_1/c$. Unit cell parameters were obtained by a least-squares fit to the settings for ten hand-centered reflections (Cu K*α*, λ = 1.541 78 Å).

Intensity data were collected on a Picker FACS-1 diffractometer. Procedures have been described previously.[24] A total of 2265 reflections out of a possible 2622 with $2\theta \leq 130°$ was considered nonzero at the 2*σ* level. Absorption or extinction corrections were not applied; there was no evidence for crystal decomposition.

The structure was solved by the MULTAN program.[21] Least-squares refinement, varying positional and anisotropic thermal parameters for the nonhydrogen atoms, converged to an *R* factor of 0.102 and an R_2 of 0.126. A difference map allowed the positions for all the hydrogen atoms to be assigned except for the hydroxylic protons. A diffuse volume of electron density appeared in the region corresponding to the hydroxylic hydrogen atoms, and a relatively large electron density (0.8 e/Å^3) appeared near the region of C(11), corresponding to H(11). Eleven low-order reflections[25] were removed from the data, and after further refinement a second difference map was obtained containing three peaks of 0.20 (H(1)), 0.13 (H(1′)), and 0.21 (H(2)) e/Å^3 which corresponded to chemically reasonable positions for hydrogen atoms. These hydrogen atoms were included in the calculations with half-occupancy and their thermal parameters were held constant at 4.0 Å^2.[26] After two final cycles of full-matrix least-squares refinement varying positional and anisotropic thermal parameters for all nonhydrogen atoms, positional and isotropic thermal parameters for the nonhydroxylic hydrogen atoms, and positional parameters for the three half-hydrogens, the final values of *R* and R_2 were 0.061 and 0.067. The "goodness of fit" between the observed and calculated models was 3.62. Both final *R*-factor calcu-

Table I. Final Atomic Coordinates for **1c**

atom	*x*	*y*	*z*
C(1)	0.3775(1)	0.5817(3)	0.6212(1)
C(2)	0.3182(1)	0.5024(3)	0.6321(1)
C(3)	0.2770(1)	0.4469(3)	0.5706(2)
C(4)	0.2234(1)	0.3768(4)	0.5821(2)
C(5)	0.2102(2)	0.3588(5)	0.6542(3)
C(6)	0.2502(2)	0.4130(5)	0.7159(3)
C(7)	0.3038(2)	0.4869(4)	0.7054(2)
C(8)	0.3725(1)	0.7579(3)	0.6345(1)
C(9)	0.3200(2)	0.8374(3)	0.6065(2)
C(10)	0.3161(2)	0.9979(4)	0.6186(2)
C(11)	0.3641(2)	1.0776(4)	0.6582(2)
C(12)	0.4156(2)	1.005(4)	0.6855(2)
C(13)	0.4210(2)	0.8405(3)	0.6739(2)
C(14)	0.3960(1)	0.5440(2)	0.5428(1)
C(15)	0.4146(1)	0.3932(3)	0.5294(1)
C(16)	0.4329(1)	0.3494(3)	0.4610(1)
C(17)	0.4331(1)	0.4630(3)	0.4041(1)
C(18)	0.4146(1)	0.6149(3)	0.4146(1)
C(19)	0.3960(1)	0.6522(3)	0.4845(1)
C(20)	0.4530(2)	0.1845(3)	0.4488(2)
C(21)	0.4176(3)	0.7395(4)	0.3544(2)
O(1)	0.4232(1)	0.5154(2)	0.6805(1)
O(2)	0.4550(1)	0.4182(2)	0.3374(1)
H(1)[a]	0.457(2)	0.536(4)	0.672(2)
H(2)	0.434(2)	0.454(5)	0.292(2)
H(3)	0.285(1)	0.462(4)	0.522(2)
H(4)	0.193(2)	0.336(5)	0.532(2)
H(5)	0.169(2)	0.314(4)	0.666(2)
H(6)	0.244(2)	0.405(5)	0.768(2)
H(7)	0.329(1)	0.531(4)	0.749(2)
H(9)	0.284(1)	0.779(4)	0.580(2)
H(10)	0.275(2)	1.044(4)	0.599(2)
H(11)	0.361(2)	1.190(4)	0.669(2)
H(12)	0.453(2)	1.058(5)	0.715(2)
H(13)	0.459(2)	0.788(4)	0.696(2)
H(15)	0.414(1)	0.316(3)	0.571(1)
H(19)	0.381(1)	0.753(3)	0.490(1)
H(20)A	0.496(2)	0.186(4)	0.445(2)
H(20)B	0.442(2)	0.125(5)	0.494(2)
H(20)C	0.437(1)	0.145(4)	0.401(2)
H(21)A	0.387(2)	0.718(5)	0.309(3)
H(21)B	0.412(2)	0.845(5)	0.372(2)
H(21)C	0.448(2)	0.727(6)	0.327(3)

[a] Hydrogen atoms are given the numbers of the atoms to which they are bonded.

Table II. Final Atomic Coordinates for **1a**

	x	*y*	*z*
C(1)	0.9286(3)	0.9653(1)	0.7702(2)
C(2)	0.8285(3)	1.0425(1)	0.7170(2)
C(3)	0.7418(3)	1.0432(2)	0.5959(2)
C(4)	0.6550(4)	1.1153(2)	0.5489(3)
C(5)	0.6511(4)	1.1872(2)	0.6214(4)
C(6)	0.7394(4)	1.1882(2)	0.7440(4)
C(7)	0.8259(3)	1.1171(2)	0.7890(3)
C(8)	1.0990(3)	0.9824(1)	0.7748(2)
C(9)	1.1508(3)	1.0474(2)	0.7039(2)
C(10)	1.3067(4)	1.0607(2)	0.7096(3)
C(11)	1.4143(3)	1.0118(2)	0.7858(4)
C(12)	1.3664(4)	0.9464(2)	0.8573(4)
C(13)	1.2096(3)	0.9314(2)	0.8514(3)
C(14)	0.8743(2)	0.8816(1)	0.6968(2)
C(15)	0.7371(3)	0.8422(2)	0.7123(2)
C(16)	0.6837(3)	0.7673(2)	0.6491(2)
C(17)	0.7664(3)	0.7302(1)	0.5677(2)
C(18)	0.8990(3)	0.7700(2)	0.5465(2)
C(19)	0.9522(3)	0.8447(2)	0.6117(2)
O(1)	0.9117(2)	0.9502(1)	0.8985(2)
O(2)	0.7115(2)	0.6542(1)	0.5093(2)
H(01)[a,b]	0.830(6)	0.958(4)	0.890(5)
H(01)[b]	0.933(5)	1.000(3)	0.936(4)
H(02)[b]	0.809(5)	0.626(3)	0.449(4)
H(02′)[c]	0.591(0)	0.634(0)	0.545(0)
H(3)	0.752(3)	0.991(2)	0.545(2)
H(4)	0.583(4)	1.118(2)	0.472(3)
H(5)	0.584(3)	1.239(2)	0.595(3)
H(6)	0.748(4)	1.240(2)	0.805(3)
H(7)	0.884(3)	1.115(2)	0.875(3)
H(9)	1.069(3)	1.084(2)	0.642(3)
H(10)	1.337(4)	1.108(2)	0.662(3)
H(11)	1.559(2)	1.021(1)	0.818(2)
H(12)	1.445(4)	0.904(2)	0.911(3)
H(13)	1.172(3)	0.879(2)	0.893(3)
H(15)	0.680(3)	0.870(2)	0.769(2)
H(16)	0.586(3)	0.741(2)	0.662(2)
H(18)	0.959(3)	0.748(2)	0.496(2)
H(19)	1.042(3)	0.868(1)	0.603(2)

[a] Hydrogen atoms are given the numbers of the atoms to which they are attached. [b] These atoms were included with an occupancy of 0.5. [c] This atom was not included in the structure factor calculations, but is a possible site for the disordered H(O2). See supplementary text.

lations and also the "goodness-of-fit" calculations included all the nonzero reflections of the data set.[27,28] The atomic scattering factors of Cromer and Mann[29] and that of Stewart, Davidson, and Simpson[30] were used for all nonhydrogen atoms and hydrogen atoms, respectively, in the structure factor calculations. The final coordinates for **1a** are given in Table II. The final values of the thermal parameters and of the structure factors have been deposited.[23]

X-ray Powder Photography. Debye-Scherrer powder photographs were taken with a camera manufactured by Charles Supper Co., using Ilford Type G film and nickel-filtered Cu Kα radiation (λ = 1.541 78 Å). A freshly ground sample of the hydroxyphenol **1c** (recrystallized from ether-hexane) gave a photograph showing spacings in agreement with those calculated[31] from the crystal data of **1c**. The powder photograph of fuchsone **2c** obtained by heating a microcrystalline sample of **1c** for 48 h at 110 °C was identical with a photograph of a pseudomorph obtained by heating a single crystal of **1c** for 7 days at 110 °C (without grinding) except that the latter photograph showed streaking indicating some residual order. The *d* spacings obtained from both photographs agreed with those calculated from crystal data for the $\beta(P2_12_12_1)$ form of **2c**.[31,32]

Single Crystal Experiments. All thermal and photochemical experiments were conducted with samples with a satisfactory elemental analysis (±0.3). Single crystals of light-sensitive compounds were grown by slow evaporation of a solution protected from light by aluminum foil.

Quantitative Studies of the Dehydration of the Dimethyl Alcohol (1c) and Dibromo Alcohol (1b). The extent of the dehydration of single crystals of **1b** and **1c** was determined by UVANL, a computer program based on the Dewar-Urch method of UV analysis.[33] The measurements at the 28 wavelengths utilized in UVANL were made every 5 nm from 255 to 390 nm in the spectra of the mixtures of **1c** and **2c** and at 39 wavelengths (every 5 nm) over the range 260–450 nm for mixtures of **1b** and **2b**. Agreement to ±3% was found using four samples of known composition, the ratios of **1**:**2** varying from 30:70 to 80:20.

The rate data presented in Figure 1 were obtained using single crystals of both habits of **1c**; crystals were chosen which appeared to be without major defects and of approximately the same size. Twenty to thirty single crystals were placed on a microscope slide and the slide placed on a calibrated Kofler hot stage (preheated to 110 ± 2 °C). As the crystals were removed at the times indicated, they were analyzed individually (without further purification) by dissolution in diethyl ether in a UV cell. The UV spectra thus obtained were analyzed for percent reaction by UVANL. Each point in Figure 1 represents the analysis of one crystal. The data presented for both **1b** and **1c** are a composite of two such experiments.

Similar experiments conducted with single crystals of both **1b** and **1c** which were heated at 110 °C for various times and then analyzed for percent reaction by elemental analysis gave results in good agreement with those above.

Single crystals (~50 mg) of **1c** were heated at 110 °C for 10 days and then analyzed without further purification by NMR. The spec-

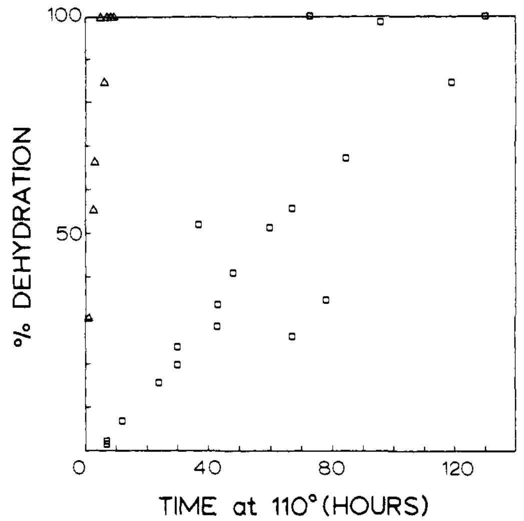


Figure 1. Comparison of the thermal rates of dehydration of (3,5-dimethyl-4-hydroxyphenyl)diphenylmethanol (**1c**) (□) and (3,5-dibromo-4-hydroxyphenyl)diphenylmethanol (**1b**) (△), single crystals at 110 °C. Each point represents the analysis of one single crystal heated for the time indicated.

trum thus obtained was identical with the NMR spectrum of an authentic sample of **2c**. Similarly **1b**, after being held at 110 °C for 24 h, gave an NMR spectrum and mp 236° C (lit. 236-238 °C), identical with that of **2b**.

The irradiation of single crystals of **1c** was conducted using either a Mineralight UVSL-25 TLC indicator lamp (λ 254 nm)[34] at a distance of 2.5 cm or a Rayonet photochemical reactor (high intensity,[35] λ 254 nm). The UV spectrum of a very concentrated solution in diethyl ether of a single crystal of **1c** which had been irradiated for 48 h with a Mineralight lamp showed a slight absorption at ~360 nm, which corresponds to the λ_{max} of **2c**. The concentration of **2c** was too small ($\ll$1%) to permit analysis by UVANL. Three single crystals irradiated for 48 h with a Mineralight lamp and heated for 10 min were shown by analysis to be 0.8, 1.1, and 2.0% reacted.

The surface nature of the photochemical reaction was demonstrated by painting all but one face of several large single crystals of **1c** (habit II) prior to irradiation with Perfex Corp. Black Opaque. The exposed face was irradiated for one day in the Rayonet photochemical reactor and the Black Opaque washed off with water. Microscopic examination showed that only the exposed crystal face had the yellow coloration indicative of reaction. No coloration in the interior portions of the crystal was observed. Subsequent heating of such a crystal resulted in preferred thermal reaction on the previously irradiated face.

Single crystals of **1c** of high quality may be kept in the dark at ambient temperature for 6 months or longer without any evidence of dehydration, but even in the dark they eventually began to show yellow coloration due to the thermal reaction. After several months at ambient temperature in the dark, irradiated single crystals, which had displayed good extinction properties under crossed-polarized light immediately after irradiation, further reacted to such an extent (~1-2%) that they no longer displayed extinction properties of a single crystal. Powdered samples of **1c** (white) may be kept in the refrigerator in the dark for long periods of 1 year or more without showing any indication of dehydration.

The photonucleated thermal reactions of **1b** and **1c** were conducted by positioning a thin strip of aluminum foil such that only a portion (~50%) of the top surface of the crystal was exposed to light. After irradiation for 48 h with the Mineralight lamp the crystals were heated on the Mettler hot stage. The effect of preirradiation on the thermal reaction of crystalline **1c** was observed on crystals which were irradiated for 48 h or less; even crystals which showed no yellow coloration due to the preirradiation underwent an accelerated thermal reaction. In general, the shorter the period of irradiation, the less dramatic were the effects of the light-nucleated reaction upon heating. Single crystals of **1c**, irradiated with the Mineralight lamp for a much longer period (170 h), displayed the same behavior as crystals irradiated for 48 h, suggesting an upper limit for the effect of the preirradiation. Qualitatively similar behavior was observed with the dibromocarbinol **1b**.[36]

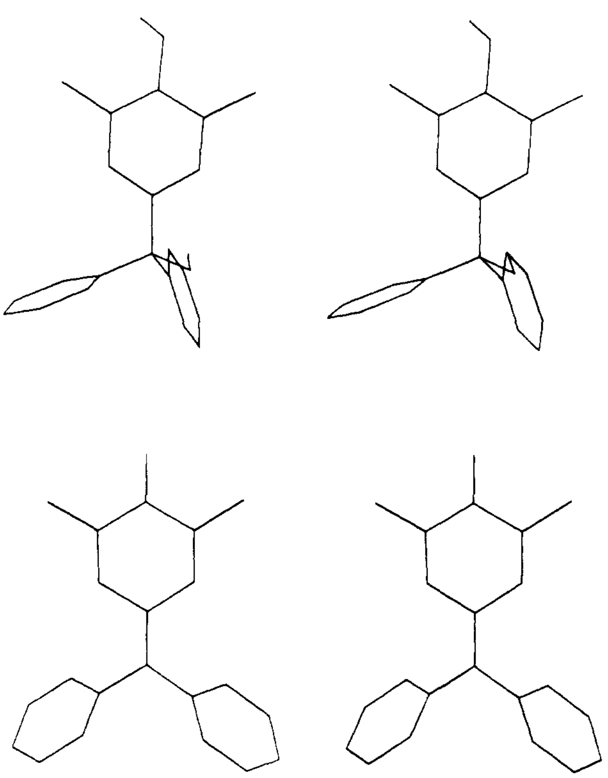


Figure 2. Stereopair drawings showing the change in molecular shape when **1c** is dehydrated to **2c**. The upper drawing in molecule **1c** is taken from data of this paper; the lower drawing of **2c** is based on data of ref 32.

Acid-catalyzed initiation experiments (similar to those reported by Puckett, Paul, and Curtin[7]) were conducted by placing a small pile of *p*-toluenesulfonic acid crystals next to a single crystal of **1b** on a microscope slide and heating to 110 °C. The reaction was initiated at points on the single crystal closest to the acid. Moving the pile of acid next to another face of the crystal resulted in the same behavior. Thus, the acid initiation seemed to depend primarily on the degree of exposure of a crystal face to the acid vapors.

The thermal reaction of **1b** at 110 °C of a single crystal immersed in Dow-Corning 200 oil proceeded in the same fashion as without the oil. Pricking a crystal of **1b** with a pin, followed by heating at 110 °C failed to produce a dramatic effect on nucleation of the reaction, although the reaction did seem to take place initially at the defect, followed by thermal reaction in the remaining portions of the crystal.

Single crystals of **1b**, obtained by slow evaporation of an ether-hexane solution, contained, in some cases, very small amounts of **2b** as indicated by a light yellow coloration. Even when precautions were taken, absolutely colorless crystals of **1b** were very difficult to obtain. Single crystals of **1b** stored in the dark at ambient temperatures invariably developed a slightly yellow color. Many of the experiments utilizing single crystals of **1b** were conducted with such crystals containing a very small amount of the dehydration product, **2b**. These crystals showed the same gross chemical reactivity as the colorless crystals. Samples of white, microcrystalline **1b** could be stored in the refrigerator (in the dark) without any coloration due to dehydration.

Results and Discussion

Thermal Dehydration. Microcrystalline powders of the hydroxytriphenyl **1a** were found to give fuchsone **2a** on heating as had been reported in the previous literature.[17] The determination of the crystal structure of **1a** by X-ray diffraction showed that the phenolic hydroxyl groups were hydrogen bonded to the alcoholic hydroxyls as had been anticipated. However, the hydrogen bonding was complicated by disorder of the hydroxylic protons. Furthermore, although it was possible to grow very small and well-formed "cube-shaped"

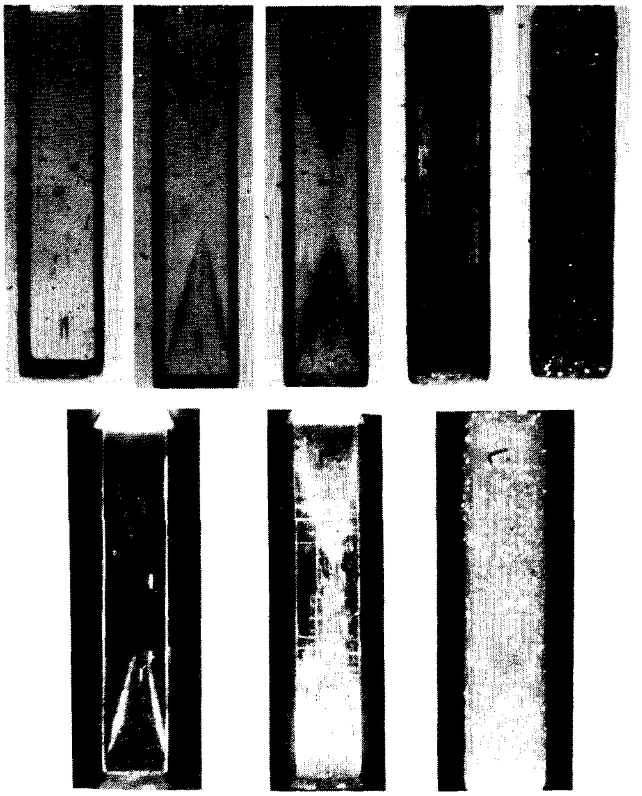


Figure 5. A crystal of habit I of **1c** undergoing thermal dehydration at 110 °C. The crystal dimensions are approximately 3.1 × 0.7 × 0.1 mm. The upper row of photographs was taken (from left to right) at times of 0, 1.8, 5.5, 8.0, and 32.5 h with illumination from beneath the crystal. The bottom row of photographs was taken with the crystal initially in the extinction position between crossed polarizing filters at times (from left to right) of 1.8, 5.5, and 32.5 h.

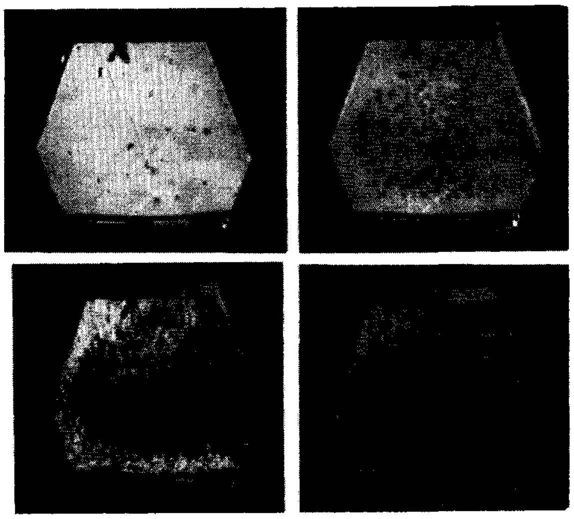


Figure 6. Reaction at 110 °C of a single crystal (habit II) approximately 1.0 × 0.85 × 0.1 mm initially in the position of maximum extinction between crossed polarizing filters. Upper left $t = 0$, right 15 min. Lower left 70 min, right 185 min.

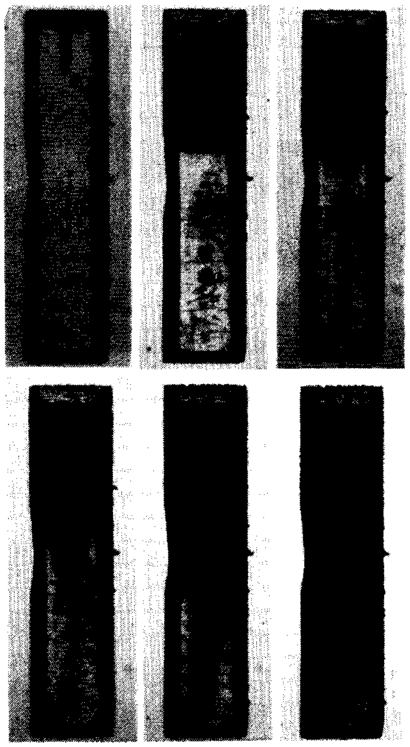
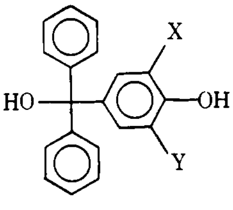


Figure 7. Photonucleated thermal reaction of a crystal of **1c** ca. 2.7 × 0.6 × 0.1 mm. Upper left: top third of crystal irradiated until faintly yellow. Upper middle: same crystal heated for 10 min at 110 °C. Upper right: crystal after 20 min. Bottom: left to right heating times 30, 45, and 60 min at 110 °C.



3a, X = CH_3; Y = H
b, X = CH_3; Y = Br

similar. However, it should be noted that it had been reported by Gomberg and van Stone[15] that, based on casual observation and measurement of the rate of evolution of water vapor when the crystals were heated, the monomethyl compound **3a** had undergone 30% dehydration in 3 days at 70 °C whereas the bromomethyl compound **3b** had not undergone measurable reaction in the same time at 75 °C. Since crystal structures of **3a** and **3b** have not been determined, it cannot be said whether it will be possible to sort out effects of crystal packing from electronic effects and the effects of molecular geometry.

Photochemical Dehydration. It had been reported by Gomberg[17] that **1a** in powdered form was converted to fuchsone **2a** on irradiation with sunlight, the reaction occurring in the top layer of the powder. Both **1b** and **1c** were found to undergo a change in color corresponding to conversion to the fuchsone when irradiated with a low-intensity UV source (low-pressure mercury lamp with radiation at 254 nm). In fact "photographic prints" could be made by saturating a piece of filter paper with a solution of **1b** or **1c**, drying, and exposing with a UV light source through a black mask with letters cut out of it. A crystal of **1b** (or **1c**) when irradiated on its major face became orange (or yellow) and opaque. Spectroscopic analysis showed that the surface of a crystal of **1c** appeared uniformly yellow and opaque after less than 1% conversion to fuchsone **2c** had occurred. A single crystal of **1c**, covered except for one face with an opaquing medium and exposed to UV light on the uncoated face, showed on removal of the opaquing medium that reaction had been limited to a thin layer near the exposed surface in agreement with the observations made by Gomberg with powdered **1a**. The extinction coefficients of starting material **1c** and product **2c** are comparable (ϵ 1200 and 1400, respectively, in ether solution at 254 nm, the wavelength of the radiation employed); the details of the mechanism of the photochemical process require much more investigation.

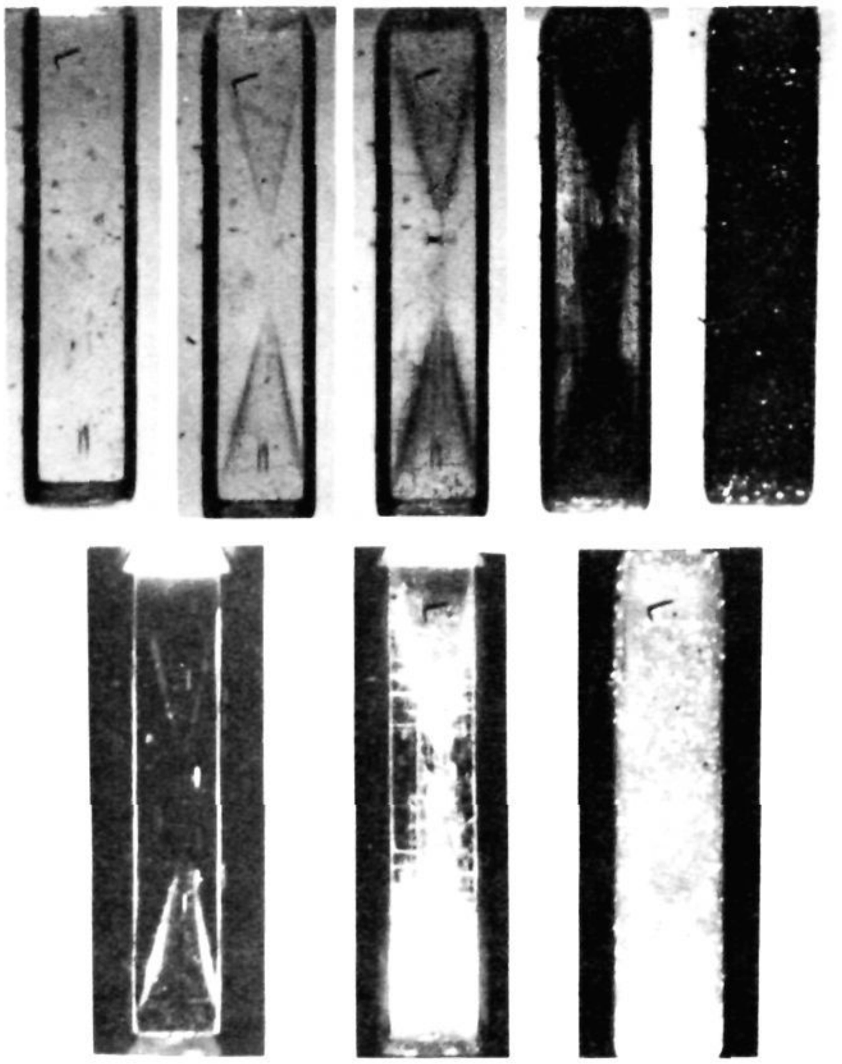
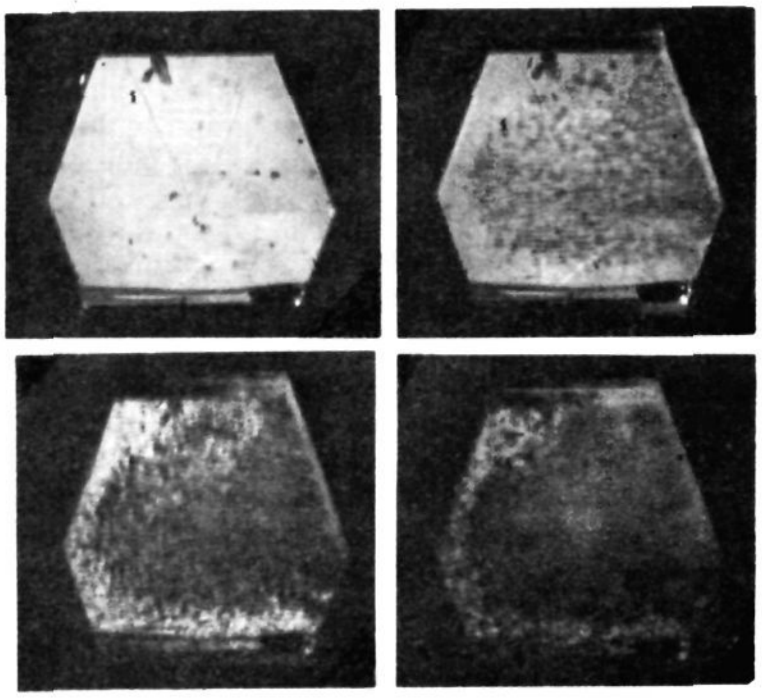


Figure 5. A crystal of habit I of **1c** undergoing thermal dehydration at 110 °C. The crystal dimensions are approximately 3.1 × 0.7 × 0.1 mm. The upper row of photographs was taken (from left to right) at times of 0, 1.8, 5.5, 8.0, and 32.5 h with illumination from beneath the crystal. The bottom row of photographs was taken with the crystal initially in the extinction position between crossed polarizing filters at times (from left to right) of 1.8, 5.5, and 32.5 h.



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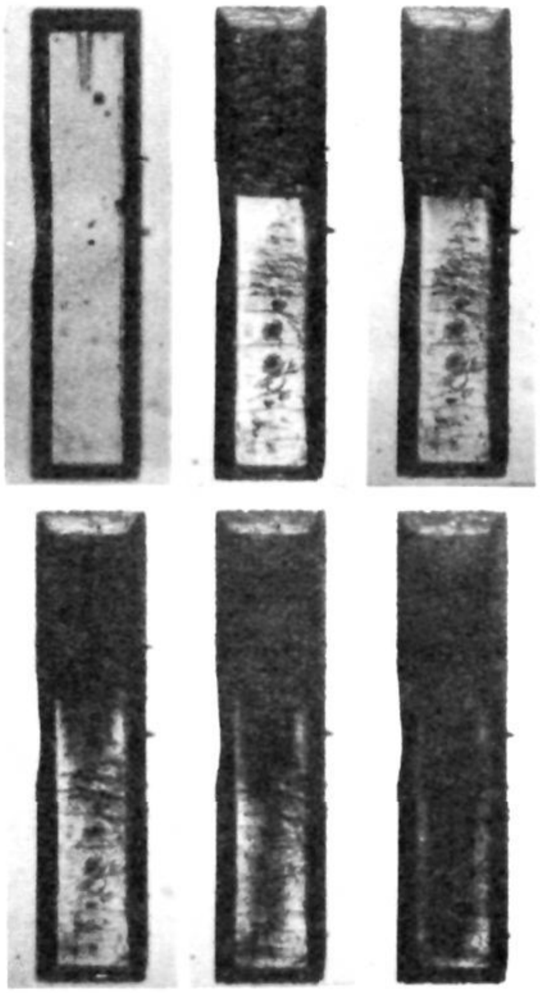

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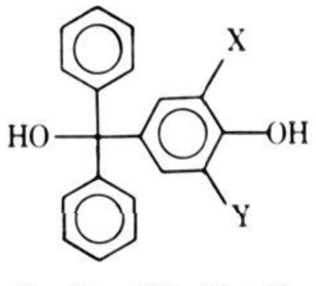

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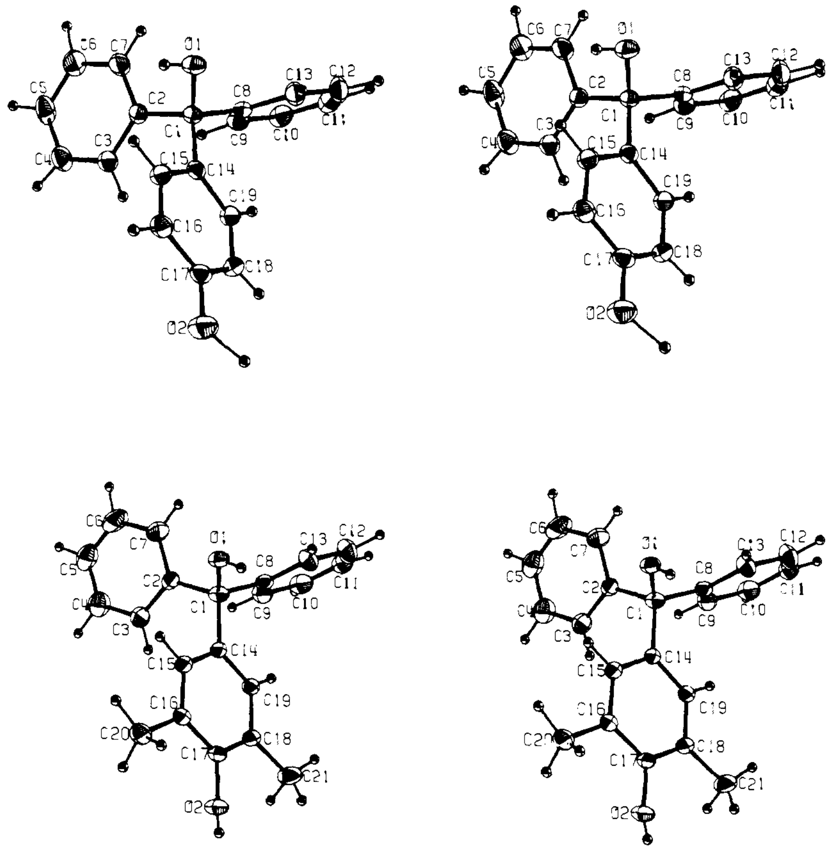

Figure 8. Stereoscopic views of single molecules of (top) **1a** and (bottom) **1c**. In **1a**, only one position for the disordered hydroxyl hydrogen atoms is shown.

However, studies of the solution photochemistry of phenols have established that the lowest singlet excited state of phenol has an acidity which is some six powers of ten greater than the acidity of phenol in the ground state.[40,41] Attempts have been made to take advantage of the enhanced acidity by using the excited phenol as a catalyst of solution reactions.[42] The implications for the solid-state dehydration of the increased acidity of photoexcited phenol are clear, and the mechanism deserves further study.

Photonucleated Thermal Dehydration. The most interesting aspect of the dehydration of hydroxyarylcarbinols **1** to fuchsones **2** has been the demonstration that the photochemical reaction could serve to produce nucleation sites for the thermal reaction. In Figure 7 is shown a crystal of habit I of the dimethyl compound, **1c**, a part of which was exposed to UV light prior to heating. The exposed section of the crystal clearly showed a much greater thermal reactivity than the remainder. The emergence of streamers of reaction from the irradiated region (Figure 7) again indicates the preference for reaction along the direction of hydrogen-bonded chains. Both habit II of **1c** and the dibromo compound **1b** showed nucleation of the thermal reaction, but without the emergence of streamers described above for habit I of **1c**. The precise nature of the nucleation process is unclear. It appears possible that disordering of crystal sites by formation of clusters of critical numbers of molecules of the product fuchsone is the source of nucleation. It is relevant that Gomberg and others had isolated, in addition to the colorless forms of phenol carbinols such as **1**, yellow forms which had lower melting points and which were believed to be "quinoid" isomers. The resulting controversy over whether two forms existed was resolved years later[8,9] by the demonstration that the second "colored form" was the colorless phenol carbinol **1** containing a small amount (even as little as 1% or less) of fuchsone **2** formed by dehydration.

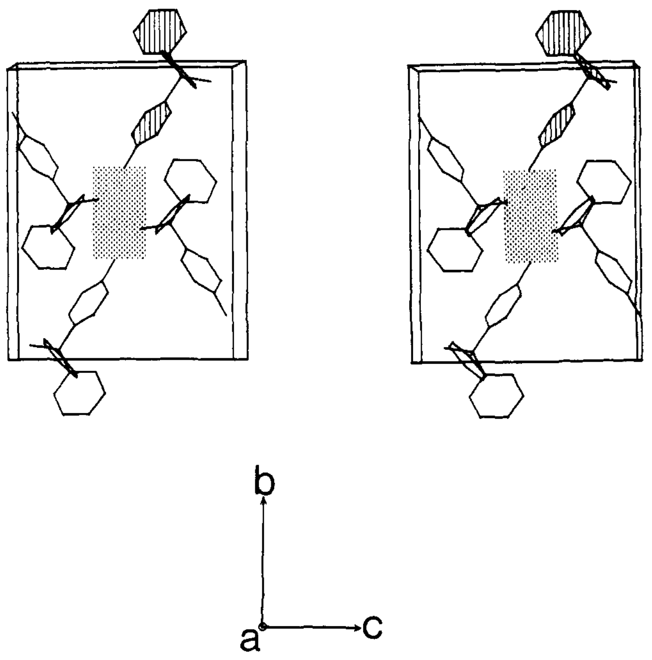

Figure 9. Stereopair drawing of the unit cell of **1a**. The reference molecule is shaded. The disordered hydroxylic hydrogen atoms are omitted but the region of hydrogen bonding is indicated by the dotted plane in the middle of the cell.

One of Gomberg's main pieces of evidence for the structure advanced for the "yellow form" had been that measurements of the rates of elimination of water from the crystalline powders showed that the "yellow form" reacted faster than the colorless. It seems likely, then, that the more reactive "yellow forms"

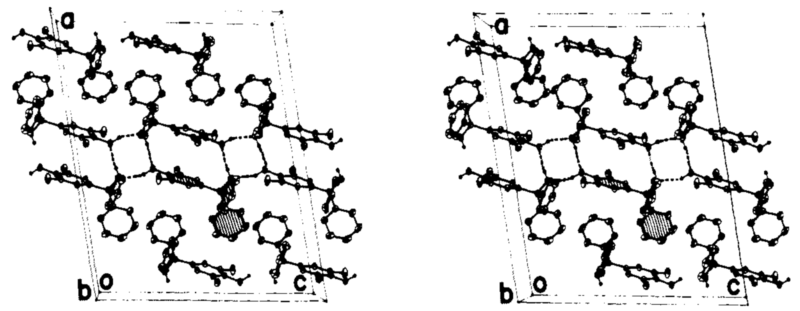

Figure 10. Stereopair drawing of the contents of one unit cell of the dimethylphenol **1c**. The reference molecule is shaded. Hydrogen bonds are shown by discontinuous lines.

studied by Gomberg and his collaborators[15,17] were solid solutions of the fuchsone product **2** incorporated into the phenol starting material **1** during crystallization and that the presence of such fuchsone molecules provided nuclei for initiation of the solid-state dehydration.[43] Thus, explanation of the photonucleation may require nothing more than the postulation of production of nucleation sites by photolytic formation of fuchsone in the crystal of carbinol. Whether the effect of the incorporation of fuchsone molecules is through chemical action such as acceptance of a phenolic proton to initiate a chain dehydration, or through introduction of lattice defects, or by some other mechanism remains to be seen.

It has been convenient to classify thermal solid-state reactions of organic compounds in terms of two limiting mechanisms, "heterogeneous" and "homogeneous",[1b] usage similar to that previously employed by Wegner and his associates[44] in discussing the polymerization of diacetylenes. The heterogeneous reaction is characterized by nucleation followed by migration in a reaction front (or fronts) through the crystal. The controlling feature is thus the nucleation process and an understanding of how to control this part of the reaction has in general been elusive. Although thermal dehydration of carbinols such as **1** shows both homogeneous and heterogeneous stages, it is of particular interest that it is the first reaction of this type where such complete control of nucleation is attainable.

Molecular Structures of the Carbinols 1a and 1c. The bond lengths and angles found in these compounds are in agreement with those reported previously for corresponding dimensions. Stereoscopic views of the two molecules are shown in Figure 8. There has been considerable interest in the disposition of three aryl groups attached to a single carbon center.[45] Details of these aspects of the geometry of **1a** and **1c** along with some comparisons can be found in the microfilm edition and in ref 1a.

Crystal Structures of 1a and 1c. The predominant feature of both crystal structures is hydrogen bonding involving the phenolic and alcoholic groups. In the crystal of **1a**, the hydrogen bonding forms a two-dimensional net in the *bc* plane. The contents of a unit cell in the crystal of **1a** are shown in Figure 9. The distance between the phenolic hydroxyl oxygen atom in the reference molecule and the alcoholic oxygen atom in the molecule at x, $1\frac{1}{2} - y$, $-\frac{1}{2} + z$ is 2.825 (3) Å, while the distance between that alcoholic oxygen atom and the centrosymmetrically related one in the molecule at $2 - x$, $-\frac{1}{2} + y$, $1\frac{1}{2} - z$ is 2.876 (3) Å. The relative geomery of these atoms is consistent with hydrogen bonding between the phenolic oxygen atom and the alcohol oxygen atom and between the two alcohol oxygen atoms related by the center of symmetry. However, the centrosymmetric character of the crystals, supported by the discovery of two positions for each hydrogen atom, requires a statistically disordered arrangement of hydrogen atoms. In half of the unit cells in the crystal the hydrogen-bonding pattern is O(phenol) (reference)-H- - -O (alcohol) (x, $1\frac{1}{2} - y$, $-\frac{1}{2} + z$)-H- - -O (alcohol) ($2 - x$, $-\frac{1}{2} + y$, $1\frac{1}{2} - z$)-H- - -O (phenol) ($2 - x$, $1 - y$, $1 - z$), with the hydrogen of this last phenolic oxygen not involved in any hydrogen bonding, while in the other half of the cells the hydrogen-bonding pattern as regards donors and acceptors is exactly reversed and the hydrogen atom of the phenolic oxygen in the reference molecule is not involved in hydrogen bonding. The probable alternative site for the phenolic proton raises the possibility of a very weak O-H- - -aromatic hydrogen bond (see supplementary text). The shading in Figure 9 shows the region where the disordered hydrogen atoms would be. Further details of the hydrogen bonding in **1a** can be found in the microfilm edition and in ref 1a.

The crystal structure of **1c** is not complicated by disorder in the positions of the hydroxyl hydrogen atoms. The packing is shown in Figure 10. The molecules are linked by hydrogen bonds to form double chains that run along the *c* axis. These double chains are formed by four oxygen atoms (two of each type) lying at the corners of an approximate square with a twofold axis of symmetry normal to the plane of the square. However, as the hydrogen bonds are all along the edge of the square, there is no observable disorder in the hydrogen atoms. The alcoholic oxygen atom in the reference molecule forms a hydrogen bond to the phenolic oxygen in the molecule at $1 - x$, $1 - y$, $1 - z$; the O- - -O and H- - -O distances are 2.853 (3) and 2.04 (4) Å, respectively, and the C-O- - -O and O-H- - -O angles are 114.8 (1) and 174 (4)°, respectively. The phenolic oxygen forms a hydrogen bond to the alcoholic oxygen in the molecule at $1 - x$, y, $1\frac{1}{2} - z$; the O- - -O and H- - -O distances are 2.792 (2) and 1.95 (4) Å, respectively, and the C-O- - -O and O-H- - -O angles are 134.8 (1) and 152 (4)°, respectively. The "square" is completed by the two hydrogen bonds related by the symmetry axis passing through the center.

Supplementary Material Available: Additional discussion and tables of thermal parameters, bond lengths, bond angles, intermolecular contacts, and observed and calculated structure factors for **1a** and **1c** (49 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Taken from the Ph.D. Thesis of Terry W. Lewis submitted to the University of Illinois, 1977, available from University Microfilms, Ann Arbor, Mich. (b) Preliminary presentations of portions of this work have been published [T. W. Lewis, S. A. Puckett, D. Y. Curtin, and I. C. Paul, *Mol. Cryst. Liq. Cryst.*, **32**, 111 (1976); D. Y. Curtin, I. C. Paul, E. N. Duesler, T. W. Lewis, B. J. Mann, and W.-I. Shiau, *ibid.*, **50**, 25 (1979).

(2) We are indebted to the National Science Foundation (NSF DMR 7203026) for support of this work.

(3) (a) D. Y. Curtin, I. C. Paul, E. N. Duesler, T. W. Lewis, B. J. Mann, and W.-I. Shiau, *Mol. Cryst. Liq. Cryst.*, **50**, 25 (1979); (b) J. M. Thomas, S. E. Morsi, and J. P. Desvergne, *Adv. Phys. Org. Chem.*, **15**, 63 (1977); (c) R. Lamartine, G. Bertholon, M.-F. Vincent-Falquet, and R. Perrin, *Ann. Chim.* (Paris), 131 (1976).

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therein.

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(11) See H.-D. Becker and K. Gustafsson, *J. Org. Chem.*, **41**, 214 (1976), for the procedure as applied to analogous compounds.

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(23) See paragraph at end of paper regarding supplementary material.

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(25) These reflections were 011, 013, 112, 012, 110, 141, 120, $12\bar{2}$, $10\bar{2}$, $10\bar{4}$, and 204. They were restored to the data set for the calculation of the final R factors.

(26) Attempts to refine the thermal parameters of the half-hydrogen atoms led to unreasonably high values.

(27) The large electron density maximum for H(11) (0.8 e/Å^3 compared to 0.4–0.6 e/Å^3 for the other hydrogen atoms) merits some further discussion. When a hydrogen atom was included at this position and its parameters were refined, an abnormal C–H bond length of 1.26 (2) Å was obtained. Since the molecule has a near threefold axis (if the phenolic hydroxyl group is neglected), it appeared probable that the molecule had crystallized with the three rings interchanged in a few of the molecular sites. Further evidence for this type of disorder came from the low isotropic thermal parameter for H(11) of 2.0 (3) Å^2 compared to values ranging from 3.6 to 8.1 Å^2 for the other aromatic hydrogen atoms. As the extent of the disorder appeared to be slight since the isotropic thermal parameter for O(2) was no larger than those of the rest of the nonhydrogen atoms at that stage of the refinement, no attempt was made to take account of this possible disorder in the refinement. The hydrogen atom, H(5), which might have been expected to show abnormal behavior comparable to H(11), behaved in a normal fashion. Some involvement of the ring containing H(5) in this disordered model might be indicated, however, by the residual electron density of 0.2 e/Å^3 in the region of H(5) on the final difference map.

(28) The position found for H(1) requires a disordered arrangement in the hydrogen bonding involving that atom. The hydrogen-bonding pattern also requires an arrangement for disorder in H(2). While one site for H(2) could be found, there was no definite evidence from difference maps for a second disordered site.

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(36) An additional experiment was performed with five crystals of habit I of **1c** in which all the faces except (001) were covered with the Black Opaque, followed by irradiation, removal of the Opaque, and heating at 110 °C. The irradiation of the (001) face had no pronounced effect on the observed thermal reaction of these crystals. It should be noted, however, that (1) the crystals were quite large and the nucleation of the thermal reaction occurred (yellow "triangles" of product) quite rapidly; (2) even with large crystals, it was physically very difficult to paint the crystals so that only (001) remained transparent to the irradiation.

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Thione Photochemistry. On the Mechanism of Photocyclization of Aralkyl Thiones[1]

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Abstract: The mechanism of hydrogen abstraction of aralkyl thiones to give cyclopentyl thiols has been investigated. From fluorescence measurements and the known value of k_F, the rate of hydrogen abstraction to give a 1,5-biradical has been determined. By comparison with the rate of product formation it has been shown that only about one-tenth of the biradicals, depending on the alkyl side chain, close; the rest diproportionate to give the original thione. This makes probable the existence of an intermediate (as distinct from a concerted reaction) and confirms the S_2 (π,π^*) state as the reactive state. The kinetic isotope in one instance has been determined by two routes and is about 1.6, indicating an early transition state and a very exothermic process. The activation energy for abstraction has been determined for one member of the series, **1f**, by measuring the variation of quantum yield of product and of fluorescence over a 40 °C temperature range. These results show that, although the active state is π,π^*, hydrogen abstraction occurs in a manner very similar to the alkanone type II singlet process.

It has been found[2] that excitation of the thione function, in a series of aralkyl derivatives, **1c–j**, into the S_2 (π,π^*) state[3] leads to a formal insertion into the δ position and the formation of cyclopentyl thiols **2**. The efficiency of the cyclization was not great ($\phi_{\text{cyc}} = 3.5 \times 10^{-2}$ for **1d**; $\phi_{\text{dis}} = 5.3 \times 10^{-2}$) which, *assuming the absence of a reversibly formed intermediate*, implied a rate constant for the reaction of $\sim 2 \times 10^8$ s^{-1}. No distinction could be made at that point between a concerted $2_\pi + 2_\sigma$ reaction and a process involving a short-lived biradical intermediate produced by hydrogen abstraction by the excited thione. Analogy for hydrogen abstraction by a thione π,π state now exists.[5]

The fact that in the irradiation of optically active **1i** the recovered starting material was unracemized was compatible

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