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PHOTOINDUCED REACTIONS – LXIX

THE PHOTOCHEMICAL TRANSPOSITION OF 2,6-di-t-BUTYLPHENOLS THROUGH THEIR KETONE TAUTOMERS[1]

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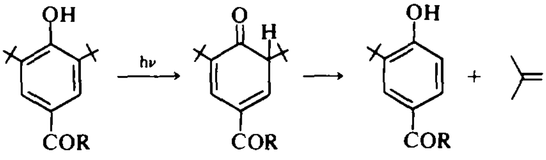
Abstract – 2,6-Di-t-butylphenol and its 4-substituted derivatives (**1**) have been shown to undergo novel photochemical transposition to isomeric phenols **2** and **3**, being accompanied by de-t-butylation to give **4**. Involvement of the triplet excited state of **1** was confirmed by sensitization and quenching experiments. Evidence is presented for the initial tautomerization of **1** to the ketonic tautomers which undergo further photochemical transformation to the products.

Simple phenols are known to undergo electron ejection or β-bond fission from their excited state to give radical species.[2] As a particular case, it was reported that 3,5-di-t-butyl-4-hydroxyphenyl ketones are photochemically de-t-butylated through the triplet state giving 3-t-butyl-4-hydroxyphenyl ketones which may be formed from a ketone tautomer intermediate.[3] In an extension of this study, we have found that certain hindered phenols, 2,6-di-t-butylphenols (**1**), undergo a unique photochemical transposition and that the reaction occurs through a ketone tautomer of the parent phenols.



Direct irradiation of 2,6-di-t-butylphenols (**1a**–**1e**) in n-hexane, methanol or acetone with light mainly at 2537 Å gave two types of rearranged products, **2** and **3**, accompanied by a de-t-butylated product **4**. The ratio of products depends upon the nature of solvent and the structural features of the starting phenols. The photoreaction could be also carried out by sensitization with acetophenone. The results are summarized in Table 1. As seen from Table 1, 2,4,6-tri-t-butylphenol (**1a**; R=t-Bu) gave only de-t-butylated products, **2a** and **4d**, but no corresponding rearranged products, **2d** and **3d**. In acetone, which can act as either a triplet sensitizer or a hydrogen acceptor in its n,π* triplet state, coupling products **5** and **6**† were obtained from **1a** and **1b** respectively, in addition to the normal transposition products. The formation of these coupling products is undoubtedly analogous to the photochemical coupling of **1a** and benzophenone reported by Becker.[4]

The acetophenone-sensitized reaction suggests that the triplet excited state of **1** may be involved in the transposition reaction. This was confirmed by a quenching experiment with a triplet quencher, piperylene, giving a linear Stern-Volmer plot (Fig 1), and by additional sensitization experiments using sensitizers having different triplet energy and triplet state configuration (n,π* or π,π*). The result shown in Table 2 indicates that the reaction can be sensitized by either n,π* or π,π* triplet sensitizers, and that the triplet energies of 2,6-di-t-butylphenols having an electron-donating group at position 4 may be around 67 kcal/mole. The value is relatively low comparing with the triplet energies of phenol (81·5 kcal/mole[5]) and of hydroquinone (74·8 kcal/mole[5]), probably due to the lowering effect of electron-donating group as seen in those of alkyl homologs of benzene.[5]

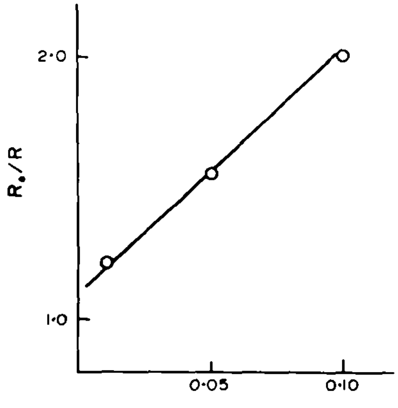


Fig 1. The plot of R_0/R against [Q].

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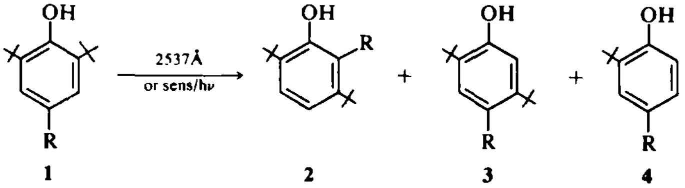
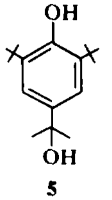
†Similar products were also detected in the acetophenone- and benzophenone-sensitized photolysis of **1a** and **2a**, but were not examined in detail.

Table 1. Sensitized and unsensitized photolysis of 2,6-di-t-butylphenols (1)



1	Solvent	Sensitizer	Light source[a]	Irad. time (hr)	Products (% yield)[b] 2	3	4	Others
	n-hexane	–	LP	31	2a = 3a (41)		4a (SA)	
1a	MeOH	–	LP	18	2a = 3a (16)			
(R=H)	acetone	*c*	LP	123	2a = 3a (4)			5 (1)
	n-hexane	acetophenone	HP	3·3	2a = 3a (4·1)		4a (2)	
	n-hexane	–	LP	35	2b (28)	3b (SA)	4b (SA)	
	MeOH	–	LP	74·5	2b (SA)	3b (10)		
1b		–	LP	120	2b (SA)	3b (10)	4b (SA)	
(R=Me)	acetone	*c*	LP	83	2b (15)	3b (SA)		6 (16)
	n-hexane	acetophenone	HP	16·5	2b (33)		4b (19)	
	MeOH	acetophenone	HP	2	2b (ND)	3b (ND)	4b (ND)	
	n-hexane	–	LP	46	2c (10)	3c (7)		
	MeOH	–	LP	67·5	2c (1·5)	3c (6·5)		
1c	acetone	*c*	LP	19·5	2c (11)	3c (6·7)		
(R=OMe)	n-hexane	acetophenone	HP	2	2c (29)	3c (7)		
	MeOH	acetophenone	HP	7		3c (19)		
	n-hexane	–	LP	30	2a (10)		4d (SA)	
1d	MeOH	–	LP	77	*d*			
(R=t-Bu)	acetone	*c*	LP	250	2a (5)		4d (SA)	
	n-hexane	acetophenone	HP	1·5	2a (SA)		4d (48)	
1e (R=OH)	n-hexane	–	LP	26	2e (31)			

[a] LP: a 10 W low-pressure mercury lamp (Vycor housing). HP: a 100 W high-pressure mercury lamp (Pyrex housing).
[b] Yields were based on the reacted starting material. SA: small amount. ND: not determined.
[c] Acetone might act partly as sensitizer.
[d] An intractable product mixture containing some starting material was obtained.



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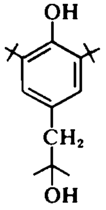

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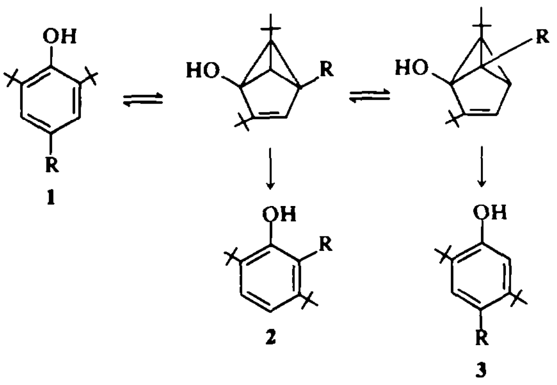
At first sight, the formation of the rearranged products **2** and **3** appeared to be rationalized by a mechanism involving benzvalene intermediates (Scheme 1), as formulated for the photochemical transposition of alkylbenzenes.[6] However, this mechanism was ruled out from the following facts. (1) Irradiation of the methyl ethers of **1b** and **1d** with light at 2537 Å gave no rearranged products corresponding to **2** and **3** but largely recovered unchanged. The result is consistent with the finding that tritium-labeled anisoles undergo virtually no photochemical transposition.[7] (2) It seems difficult to ascribe the concomitant de-t-butylation to such a benzvalene intermediate. (3) Irradiation of 2,6-di-t-butylphenol (**1a**-OD) deuterated at the hydroxyl with light at 2537 Å gave 6-deuterated **2a** (**2a**-6-d) (31·5% D-content from mass spectrometry) in n-hexane and a 1 : 1 mixture of **2a**-6-d and **2a**-4-d

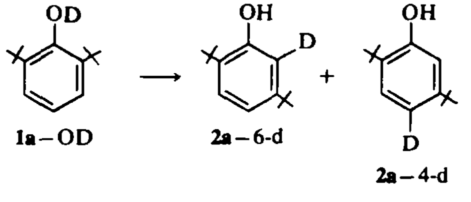
Table 2. Effects of various sensitizers on the photoreaction of 1

Sensitizer (E_T, kcal/mole)[a]	Lowest triplet state of sensitizer	Sensitization	Substrate checked (Products detected)
benzene (84·1)[c]	π,π^*	yes	1b (2b,4b); 1c (2c,3c)
acetone (80)[c]	n,π^*	yes	see Table 1
acetophenone (74·1)	n,π^*	yes	see Table 1
benzophenone (68·9)	n,π^*	yes	1b (2b, 4b)
fluorene (67·6)	π,π^*	yes	1b (2b)
triphenylene (66·6)	π,π^*	no	1b; 1c
biphenyl (65·5)[c]	π,π^*	no	1b
naphthalene (60·9)	π,π^*	no	1b; 1c
biacetyl (54·9)	n,π^*	no	1b[b]

[a] E_T values were given from data compiled by Engel and Monroe.[5]
[b] The phenol was consumed but no transposition product was detected.
[c] For these sensitizers, LP was used and for other sensitizers, HP was used.



SCHEME 1

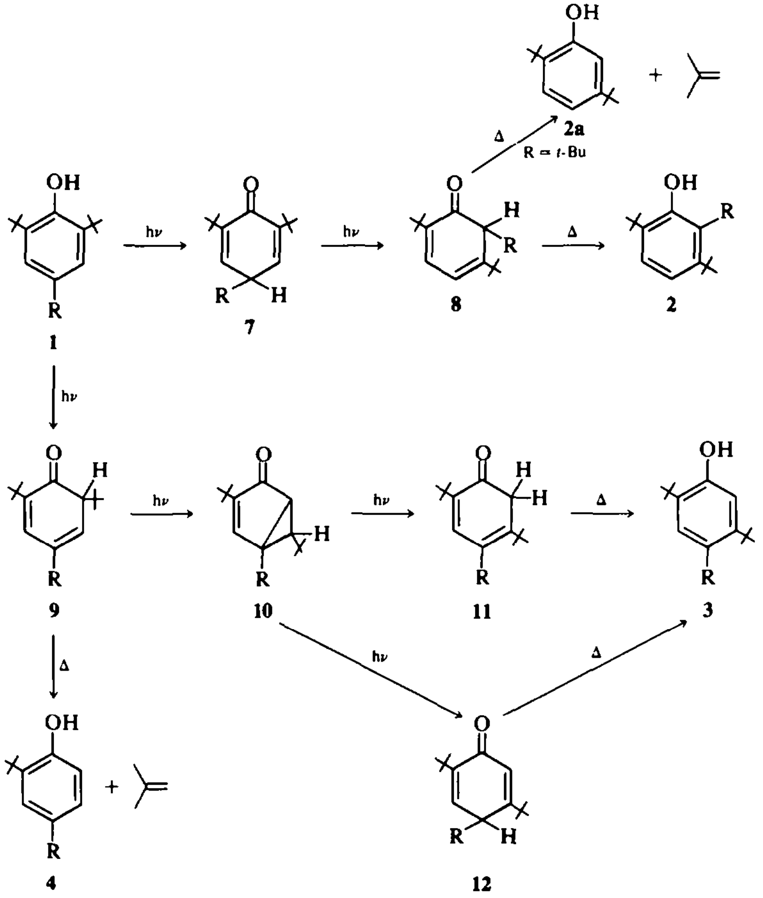


(77% D-content) in MeOD. These experiments also demonstrated that two types of transposition reactions did occur in the case of **1a** for which **2a** and **3a** could not be distinguished.

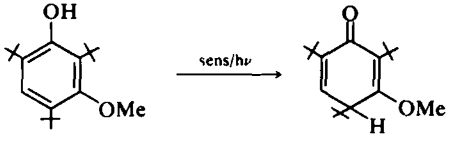
The present photo-transposition reaction can be, now, reasonably rationalized by an alternative mechanism involving ketone tautomer intermediates as formulated for the photochemical de-t-butylation of 3,5-di-t-butyl-4-hydroxyphenyl ketones.[3] (Scheme 2). According to this mechanism, ketone tautomers **7** and **9**, which are formed from the triplet state of **1**, are further photochemically transformed into **2** and **3**, respectively. *para* Ketone tautomer **7** rearranges to phenol **2** *via* its ketonic form **8** following the well-known photochemical processes for 2,5-cyclohexadienones.[8,9] *ortho* Ketone tautomer **9** photochemically rearranges, analogously to certain 2,4-cyclohexadienones,[10] to a bicyclic ketone **10**, which is in turn transformed into phenol **3** *via* either **11** or **12** following the known photochemical processes for bicyclo-[3.1.0]hexenones.[8] The concomitant de-t-butylation into **4** can be explained by considering that **9** undergoes thermal de-t-butylation. There have been several reports providing evidence that 2,5-cyclohexadienones bearing a t-butyl group at position 6 easily suffer thermal de-t-butylation.[3,11–13] The formation of **2a** from tri-t-butylphenol (**1d**) may be ascribed to thermal de-t-butylation of **8d** (R=t-Bu).

The second mechanism is strongly supported by the following facts. (1) The deuterium labeled experiments described above are consistent with this mechanism. It is noted that in this particular case the intermediates **8** and **11** should be the same. (2) Acetophenone-sensitized photolysis of a highly hindered phenol **13** with light above 3000 Å was found to give a *para* ketone tautomer **14**, which is known to be relatively stable either photochemically or thermally.[13] This provides a direct evidence for the photochemical tautomerization of hindered phenols. It may be noteworthy that the rate of the disappearance of **13** and the yield of **14** were markedly altered by solvent polarity. Thus, **13** disappeared slower in n-hexane than in methanol and the yield of **14** was higher in n-hexane (44%) than in methanol (5%).

Similarly, a solvent dependence was observed on the product ratio (**2**:**3**) in the photolysis of **1**. In nonpolar solvents the formation of **2** is predominant over **3**, while polar solvents the formation **3** is predominant over **2**. Although it is difficult to explain the solvent effect in detail from the available experimental data, some of the pathways of Scheme 2 appears to be influenced by solvent polarity considering from the fact that the photochemical reactions of certain cyclohexadienones are known



Scheme 2



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to be dependent upon solvent polarity in their rate or in their direction.[9, 10, 13]

For the mechanism of the initial tautomerization in the present phototransposition reaction, there may be several possibilities including deprotonation[14] in the excited state of the phenols followed by 1,3- and 1,5-proton shifts, recombination between a phenoxy radical and a hydrogen atom formed by photo-dissociation,[2] and photochemically allowed suprafacial [1,3]- and antarafacial [1,5]- (or a double suprafacial [1,3]-) hydrogen shifts.[15] However the detailed mechanism remains to be elucidated. In any case, it seems reasonable to ascribe one of the driving forces for the tautomerization to the ring strain of 2,6-di-t-butylphenols, for which the strain energy has been estimated as about 8 kcal/mole,[16] because irradiation of *p*-cresol in acetone gave no transposition product corresponding to **2**.

EXPERIMENTAL

Materials. Phenols **1a**, **1b** and **1d** are commercially available. **1e** was prepared by methylation of **1c** with dimethylsulfate in aq NaOH. **1e** was prepared by the reduction of 2,6-di-t-butyl-*p*-benzoquinone[17] with Zn and HCl.[18] 2,4,6-Tri-t-butylanisole and 2,6-di-t-butyl-4-methylanisole were prepared by methylation of **1d** and **1b**, respectively, according to the method by Miller and Margulies,[11] namely with MeI and NaH in DMSO.

Direct photolysis of **1** *with light at* 2537 Å

(a) *Compound* **1a**. A soln of **1a** (775 mg) in 230 ml n-hexane was irradiated using a 10 W low-pressure mercury lamp with Vycor housing under bubbling N_2 under cooling with tap water for 31 hr, and then the mixture concentrated *in vacuo* to a residue. This was chromatographed on silica gel (30 g) using light petroleum as eluent to give successively 170 mg of **1a**, 240 mg of **2a** and 220 mg of a brown oil from which **4a** was detected by VPC and TLC. Recrystallization of **2a** from light petroleum gave colorless needles, m.p. 119–120°, identical (IR) with an authentic sample synthesized independently (see below). IR (Nujol) 3600 cm^{-1}; *m/e* 206 (M^{-}); NMR (CCl_4) τ: 8·71 (s, 9H, t-Bu), 8·59 (s, 9H, t-Bu), 5·43 (s, 1H, OH) and 2·85–3·50 (m, 3H, aromatic H).

Similar irradiation (18 hr) of **1a** (475 mg) in 200 ml MeOH afforded 94 mg of **1a**, 60 mg of **2a** and *ca* 200 mg of a brown oil.

(b) *Compound* **1b**. Irradiation of a soln of **1b** (900 mg) in 230 ml n-hexane was carried out for 35 hr. After evaporating the solvent *in vacuo*, the residue was chromatographed on silica gel (30 g) using light petroleum as eluent to give successively 300 mg of **1b**, 170 mg of **2b** and 430 mg of a brown oil from which **3b** and **4b** were detected by VPC and TLC. Recrystallization of **2b** from light petroleum gave colorless crystals, m.p. 76–77°, IR (Nujol) 3600 cm^{-1}: NMR (CCl_4) τ: 8·59 (s, 18H, t-Bu), 7·62 (s, 3H, Me), 5·16 (s, 1H, OH), 3·13 (d, 1H, J = 8·4 Hz, aromatic H) and 2·92 (d, 1H, J = 8·4 Hz, aromatic H). (Found: C, 82·12; H, 10·94. Calc. for $C_{15}H_{24}O$: C, 81·82; H, 10·94%). The structure of **2b** was confirmed by acid-catalyzed de-t-butylation to *o*-cresol and by a sequence of degradation reactions leading to the methyl ether of **2a** (see below).

Irradiation (74·5 hr) of **1b** (950 mg) in 230 ml MeOH afforded, after silica gel (20 g) chromatography, 520 mg of **1b** and 53 mg of **3b**. Recrystallization of **3b** from light petroleum gave colorless crystals, m.p. 68–71°; IR (Nujol) 3500 cm^{-1}; NMR (CCl_4) τ: 8·66 (s, 18H, t-Bu), 7·60 (s, 3H, Me), 5·71 (s, 1H, OH), 3·18 (s, 1H, aromatic H) and 3·52 (s, 1H, aromatic H). (Found: C, 81·53; H, 11·02. Calc. for $C_{15}H_{21}O$: C, 81·82; H, 10·91%). The structure of **3b** was confirmed by NMR data and by acid-catalyzed de-t-butylation to *p*-cresol (see below).

Irradiation (120 hr) of **1b** (1·55 g) in 230 ml AcOH afforded 935 mg of **1b**, 70 mg of a mixture of **2b** and **3b**, 60 mg of **3b** and 490 mg of a brown oil from which **4b** was detected by VPC and TLC.

(c) *Compound* **1c**. A soln of **1c** (1·52 g) in 230 ml n-hexane was irradiated for 46 hr. After evaporating the solvent *in vacuo*, the residue was chromatographed on silica gel (50 g) using light petroleum as eluent to give successively 200 mg of a brown oil, 120 mg of **2c**, 500 mg of **1c** and 70 mg of **3c**. Recrystallization of **2c** from MeOH gave colorless crystals, m.p. 86–87°, which were identical with an authentic sample[13, 19] (IR). Recrystallization of **3c** from light petroleum gave colorless crystals, m.p. 100–101°, which were identical with an authentic sample[20] (IR). NMR τ: 8·66 (s, 9H, t-Bu), 8·60 (s, 9H, t-Bu), 6·20 (s, 3H, OMe), 3·40 (s, 1H, aromatic H) and 3·17 (s, 1H, aromatic H).

Irradiation (67·5 hr) of **1c** (2·6 g) in 230 ml MeOH afforded 530 mg of **1c**, 90 mg of **2c** and 130 mg of **3c**.

(d) *Compound* **1d**. A soln of **1d** (1·0 g) in 230 ml n-hexane was irradiated for 30 hr. After evaporating the solvent *in vacuo*, the residue was chromatographed on silica gel (30 g) using light petroleum as eluent to give successively 600 mg of **1d**, 100 mg of **2a** and a brown oil from which **4d** was detected by VPC and TLC.

Irradiation (77 hr) of **1d** (1·40 g) in 200 ml MeOH afforded 270 mg of **1d** and an intractable product mixture.

(e) *Compound* **1e**. A soln of **1e** (1·30 g) in 230 ml n-hexane was irradiated for 26 hr. After evaporating the solvent *in vacuo*, the residue was chromatographed on silica gel (50 g). Elution with light petroleum yielded 270 mg of a brown oil consisted of a complex mixture of products. Elution with light petroleum–benzene (10 : 1) yielded successively 250 mg of **2e** as light brown crystals, m.p. 42–45°, which were unstable to oxygen and were difficult to be purified. IR (Nujol) 3600 and 3400 cm^{-1}; NMR ($CDCl_3$) τ: 8·55 (s, 18H, t-Bu), 5·15 (broad s., 2H, OH) and 3·24 (s, 2H, aromatic H). The structure of **2e** was given from the spectral data.

Photolysis of 1 *in acetone*

(a) *Compound* **1a**. A soln of **1a** (2·0 g) in 230 ml acetone was irradiated with a 10 W low-pressure mercury lamp for 123 hr. Chromatographic separation (silica gel) of the product mixture gave 530 mg of **1a**, 52 mg of **2a**, 30 mg of **5** and 700 mg of a brown oil. Recrystallization of **5** from MeOH gave colorless crystals, m.p. 187–190°; IR (Nujol) 3600 and 3500 cm^{-1}; NMR ($CDCl_3$) τ: 8·90 (s, 6H, Me), 8·55 (s, 18H, t-Bu), 8·45 (s, 1H, OH), 4·68 (s, 1H, OH) and 2·91 (s, 2H, aromatic H).

(b) *Compound* **1b**. A soln of **1b** (5·04 g) in 230 ml acetone was irradiated 83 hr. Chromatographic separation (silica gel 150 g) of the product mixture gave 2·10 g of **1b**, 430 mg of **2b** and *ca* 1 g of **6**. Recrystallization of **6** from light petroleum gave colorless crystals, m.p. 92–93°; IR (Nujol) 3550 and 3300 cm^{-1}; NMR ($CDCl_3$) τ: 8·84 (s, 1H, OH), 8·75 (s, 6H, Me), 8·55 (s, 18H, t-Bu), 7·30 (s, 2H, CH_2), 4·90 (s, 1H, OH) and 3·0 (s, 2H, aromatic H) (Found: C, 77·44; H, 10·77. Calc. for $C_{18}H_{30}O_2$: C, 77·65; H, 10·86%).

(c) *Others*. Similarly, **1c** and **1d** were irradiated and the products were analyzed (Table 1).

Sensitization experiment

A soln of 50–300 mg of each phenol and a sensitizer (in such an amount that most of the incident light is absorbed by the sensitizer) in 100–230 ml n-hexane was irradiated for 1–18 hr. For benzene sensitization, benzene was used as solvent. For acetophenone sensitization. MeOH was also used as solvent (Table 1). The photolyzate was evaporated *in vacuo* and the residue was analyzed by TLC and VPC (Silicon DC 550, 200°, He). The results are summarized in Table 2.

Quenching experiment

Solns of 22 mg of **1b** and a known amount of *trans*-piperylene in 10 ml cyclohexane were prepared in quartz tubes. Each tube was replaced with nitrogen and irradiated externally with a low-pressure mercury lamp (Vycor housing) using a merry-go-round apparatus for 130 hr. The photolyzates were analyzed by VPC using 2,4,6-tribromophenol as an internal standard. The result is shown in Fig 1.

Photolysis of 2,6-*di-t-butyl*-4-*methylanisole and* 2,4-6-*tri-t-butylanisole*

A soln of 1 g of the titled compounds in 230 ml n-hexane or MeOH was irradiated with a 10 W low-pressure mercry lamp (Vycor housing) for 20–92 hr. Analysis of the photolyzate by IR and VPC showed most of the starting material was recovered unchanged.

Photolysis of deuterated 2,6-*di-t-butylphenol* (**1a**-OD)

(a) *In n-hexane*. A soln of 5·7 g of **1a**-OD, obtained by two recrystallizations of **1a** from 99% MeOD, in 230 ml n-hexane was irradiated with a low-pressure mercury lamp (Vycor housing) under N_2 for 40 hr. After evaporation, the residue was chromatographed on silica gel (120 g). Elution with light petroleum gave 200 mg of partially deuterated 2,5-di-t-butylphenol. Mass spectrometric [*m/e* 206 (rel. int. 100), 207 (61·6) and 208 (1·25)] and NMR analyses [peak ratio, H_3:H_4:H_6 = 10:7] showed that it mainly consisted of 31% deuterated **2a**-6-d.

(b) *In* MeOH. A soln of 1·0 g of **1a**-OD in 8 ml MeOD placed in a quartz tube was irradiated externally for 232 hr. Chromatographic separation of the product mixture on silica gel (30 g) gave 253 mg of the starting material and 15 mg of partially deuterated **2a** which was purified by sublimation. Mass spectrometric [*m/e* 206 (42·9), 207 (100) and 208 (17·4)] and NMR analyses (H_3:H_4:H_6 = 10:6:6) showed that it consisted of an equimolar mixture of 77% deuterated **2a**-6-d and **2a**-4-d. Under the same conditions, only 7% of deuterium of **2a**-OD was found to be incorporated into the benzene neucleus of the recovered **2a**.

Photolysis of **13**

A soln of 100 mg of **13** and 500 mg of acetophenone in 15 ml n-hexane, placed in a Pyrex tube was irradiated externally with a 450 W high-pressure mercury lamp for 5·5 hr. The identical procedure was done with a MeOH soln. VPC analysis of the photolyzates showed that 20·2 mg of **13** and 35 mg of **14** in n-hexane and 67·5 mg of **13** and 1·4 mg of **14** in MeOH were obtained. The product **13** was separated by VPC and shown to be identical with an authentic sample[13] (IR).

2,5-Di-t-butylphenol (**2a**)

This compound was prepared using the method of Omura and Matsuura.[21] A soln of 3·94 g of 1,4-di-t-butylbenzene and 30 ml 30% H_2O_2 aq in 200 ml acetonitrile was irradiated qith a 10 W low-pressure mercury lamp under N_2 for 5 hr. The excess of H_2O_2 was decomposed by the addition of 30 g $NaHSO_3$ under ice-cooling. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water, dried over Na_2SO_4 and evaporated. The residue was chromatographed on 100 g of silica gel. Elution with light petroleum yielded 1·95 g of the recovered starting material and 200 mg of **2a**. Recrystallization from light petroleum gave colorless needles, m.p. 119–120°. (Found: C, 80·52; H, 10·55. Calc. for $C_{14}H_{22}O$: C, 80·55; H, 10·68%).

De-t-butylation of **2b** *and* **3b**

A mixture of 100 mg of **2b**, 1 g of $AlCl_3$ and 20 ml of benzene was kept on standing at room temp overnight. The mixture was treated with ice-water and extracted with ether. The ether layer was washed with water, dried and evaporated. Distillation of the residue gave *o*-cresol identified by IR.

A mixture of 40 mg of **3b**, 0·5 g of $AlCl_3$ and 2 ml of benzene was treated in a similar manner giving *p*-cresol identified by IR.

Transformation of **2b** *into the methyl ether of* **2a**

(a) *Methylation of* **2b**. To a soln of 425 mg of **2b** in 20 ml of anhyd DMSO, 1 g of NaH was added under N_2 and the mixture was stirred for 20 min, then 4 ml of MeI was added. The mixture was treated with ice-water and extracted with light petroleum. The organic layer was washed with water and passed through a silica gel column (10 g). Elution with light petroleum gave 370 mg of the methyl ether of **2b** as an oil which was not further purified. NMR (CCl_4) τ: 8·60 (s, 9H, t-Bu), 8·57 (s, 9H, t-Bu), 7·52 (s, 3H, Me), 6·25 (s, 3H, OMe) and 2·92 (s, 2H, aromatic H).

(b) *3,6-Di-t-butyl-o-anisic acid.* To a mixture of 370 mg of the above methyl ether, 200 mg of KOH, 8 ml of water and 8 ml of pyridine was added 3·5 g of $KMnO_4$ in portions under refluxing. The mixture was acidified with dil HCl (pH 3) and after adding 5 g of Na_2SO_3 extracted with ether. Evaporation of the ethereal extract yielded 315 mg of 3,5-di-t-butyl-*o*-anisic acid. Recrystallization from light petroleum gave colorless needles, m.p. 110–114°; IR (Nujol) 2900, 1690 and 813 cm^{-1}; NMR ($CDCl_3$) τ: 8·58 (s, 9H, t-Bu), 8·55 (s, 9H, t-Bu), 6·10 (s, 3H, OMe), 2·87 (d, 1H, J = 9 Hz, aromatic H) and 2·65 (d, 1H, J = 9 Hz, aromatic H). (Found: C, 72·72; H, 9·20. Calc. for $C_{16}H_{24}O_3$: C, 72·69; H, 9·11%).

(c) *2,5-di-t-butylanisole.* A mixture of *ca* 300 mg of the above acid, 60 mg of Cu powder and 6 ml of quinoline was refluxed for 3 hr. The mixture was extracted with light petroleum and the extract was washed with dil HCl and evaporated. Distillation of the residue at 200° gave 134 mg of a colorless oil; NMR (CCl_4) τ: 8·72 (s, 9H, t-Bu), 8·69 (s, 9H, t-Bu), 6·20 (s, 3H, OMe) and 3·35–2·80 (m, 3H, aromatic H). (Found: C, 82·11; H, 11·05. Calc. for $C_{15}H_{24}O$: C, 81·82; H, 10·91%). This compound was identical with an authentic sample (IR, NMR and VPC) prepared by the methylation of **2a** with MeI in DMSO in the presence of NaH.[19]

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