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Photoinduced Reactions. XLII.[1] Homolytic Expulsion of 4-Substituent in the Photochemical Reaction of 2,5-Cyclohexadienones

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Irradiation of 2,4,6-tri-*t*-butyl-4-bromo-2,5-cyclohexadienone (X) in various solvents yielded 2,4,6-tri-*t*-butylphenol (XIII) in high yields. It was shown that 2,4,6-tri-*t*-butylphenoxy radical (XII) was formed as an intermediate and that the light of shorter wavelengths than 450 mμ accelerated the hydrogen abstraction of XII. The rate of the photochemical decomposition of X decreased in the order: *n*-hexane, *N*,*N*-dimethylformamide and acetic acid. This and the sensitized reaction suggest that the formation of XII from X may result from the *n*-π^* triplet state of X. On the other hand, irradiation of 2,4,6-tri-*t*-butyl-4-nitro-2,5-cyclohexadienone (XI) afforded 2,6-di-*t*-butyl-*p*-quinone (XV) and 2,4,6-tri-*t*-butylphenol (XIII), indicating a homolytic cleavage of the C–NO_2 bond.

2,5-Cyclohexadienones have been found to undergo two basic types of transformation on irradiation in neutral media; *i. e.*, (a) skeletal rearrangement, which furnishes bicyclo[3.1.0]hex-3-en-2-ones (the so-called "lumiketone"), and (b) expulsion of one of the 4-substituents followed by phenol formation.[2] Warszawski *et al.*[3] found that photolysis of 3-oxo-10β-hydroxy-17β-acetoxy-$\Delta^{1,4}$-oestradiene (Ia) and 3-oxo-10β,17β-diacetoxy-$\Delta^{1,4}$-oestradiene (Ib) resulted in the cleavage of the 10-substituent (hydroxyl and acetoxyl, respectively) and afforded the corresponding phenol II. It was also reported by Schuster and Polowczyk[4] that a spirodienone (III), photochemically, gave a biradical (IV), which abstracted hydrogen from the solvent to yield *p*-ethylphenol and an ether (V) as major products.

Recently, Schuster and Patel[5] reported the typical photochemical reaction of 2,5-cyclohexadienone, 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (VI), which isomerizes in benzene to form predominantly 6-methyl-6-trichloromethylbicyclo[3.1.0]hex-3-en-2-one (VII) and affords *p*-cresol as the main product in ethyl ether, and two possible mechanisms for *p*-cresol formation were postulated. If such a species as VIII is involved, it seems possible that cleavage of one of the substituents at the C-4 position would give *p*-methylphenoxy radical, leading to *p*-cresol (path A). A mechanistic alternative to the formation of *p*-cresol is hydrogen abstraction from the solvent by VIII to give the dienone ketyl radical IX (path B). Schuster and Patel suggested from their experimental data that the latter mechanism is favorable.

The present paper reports on the photochemical

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[1] Part XLI: K. Ogura and T. Matsuura, This Bulletin, **43**, 2891 (1970)

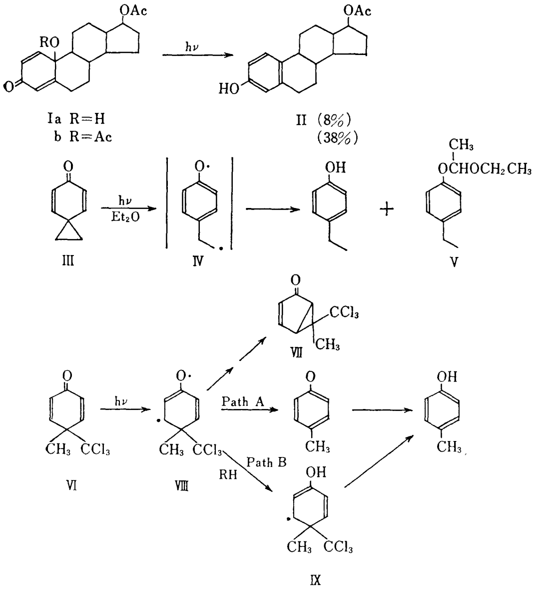
[2] For example, K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

[3] a) R. Warszawski, K. Schaffner and O. Jeger, *Helv. Chim. Acta*, **43**, 500 (1960); b) C. Ganter, R. Warszawski, H. Wehril, K. Schaffner and O. Jeger, *ibid.*, **46**, 320 (1963).

[4] D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **86**, 4502 (1964).

[5] a) D. J. Patel and D. I. Schuster, *ibid.*, **90**, 5137 (1968); b) D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968).

reactions of 2,4,6-tri-*t*-butyl-4-bromo-2,5-cyclohexadienone (X)[6] and 2,4,6-tri-*t*-butyl-4-nitro-2,5-cyclohexadienone (XI),[7] in which the process *via* path A seems preferable for the formation of 2,4,6-tri-*t*-butylphenol.



Results and Discussion

Irradiation of X in various solvents with a high-pressure mercury arc lamp filtered through Pyrex yielded 2,4,6-tri-*t*-butylphenol (XIII) in high yields (88% in ethyl ether; 81% in *n*-hexane; 56% in *N,N*-dimethylformamide; 56% in benzene). On photolysis of X in *N,N*-dimethylformamide, the solution became blue soon after the irradiation had been started. The color was extinguished by continued irradiation for a longer period of time or by bubbling oxygen. This blue solution showed a UV absorption at 630 mμ and an ESR spectrum (triplet, $a_H = 1.8$). Comparison of these spectra with those of 2,4,6-tri-*t*-butylphenoxy radical (XII), which was produced by the oxidation of XIII with lead dioxide, led us to the conclusion that the color was attributed to XII. Ultraviolet analysis indicated that the yield of the radical at a photostationary state amounted to 15%. The blue color also appeared, although weakly, on photolysis of X in *n*-hexane and benzene.

In order to see whether the recombination of the phenoxy radical XII and a bromine atom, which were produced by photolysis of X, occurs or not, X was irradiated under bubbling oxygen. It is well known that in the presence of oxygen the phenoxy radical XII was easily converted into a peroxide (XIV)[6] and that XIV was photochemically decomposed to afford 2,6-di-*t*-butyl-*p*-quinone (XV) in a high yield.[8] When a solution of X in *n*-hexane was irradiated for a short period of time with a high-pressure mercury arc lamp under bubbling oxygen, a mixture of the products, which was shown by VPC analysis to contain XV (50%) and X (6%), was obtained. However, XIII, which was formed on irradiation of X in *n*-hexane under nitrogen for the same period of time (see Table 1), could not be detected in the reaction mixture. It should be noted that the yield of the recovered X decreased remarkably in the presence of oxygen, compared with that under nitrogen. This suggests that the recombination of the phenoxy radical XII and a bromine atom may take place in *n*-hexane under nitrogen. On the other hand, it was shown that recombination was slower in *N,N*-dimethylformamide than in *n*-hexane (Table 1). This conclusion was also confirmed by the fact that the

TABLE 1. PHOTOLYSIS OF X IN VARIOUS SOLVENTS[a)]

Solvent	Irrad. time (min)	Bubbled gas	Yield (%)[b)] X	XIII	XV
n-Hexane	45	N_2	—	81(81)	—
n-Hexane	13	N_2	63	27	1
n-Hexane	14	O_2	—(6)	—	56(50)
DMF	62	N_2	—	56	7
DMF	15	N_2	77	14	—
DMF	15	O_2	59(68)	—	13(24)
Benzene[c)]		N_2		(56)	
Ether	40	N_2		(88)	
Acetic acid	60	N_2	53	15	5
DMSO	30	N_2	77	—	10

a) A solution (500 mg in 70 m*l*) of X was irradiated with a 100-W high-pressure mercury arc lamp (Pyrex filter).

b) Yields in parenthesis were obtained by VPC analysis.

c) A solution (2.00 g in 70 m*l*) of X was irradiated for 6.75 hr and bromobenzene was detected in a 4.5% yield (by VPC analysis).

TABLE 2. PHOTOLYSIS OF X[a)]

Additive	Conversion of X (%)[b)]
—	82
Naphthalene (0.203M)	84
Benzophenone (0.275M)	100

a) A solution of X in ether (0.0147M) was irradiated externally by the light of the longer wavelengths than 318 mμ.

b) by NMR analysis.

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[6] E. Müller, K. Ley and W. Kiedaisch, *Chem. Ber.*, **87**, 1605 (1954).

[7] C. D. Cook and R. C. Woodworth, *J. Amer. Chem. Soc.*, **75**, 6242 (1953).

blue color of the phenoxyl XII produced on photolysis of X in *N*,*N*-dimethylformamide (15% of the amount of the starting material X) was extinguished very slowly under bubbling nitrogen.*1 These facts and the results shown in Table 1 indicate that the primary decomposition rate of X decreases in order of *n*-hexane, *N*,*N*-dimethylformamide, and acetic acid. Since the photochemical decomposition of X was sensitized by benzophenone as shown in Table 2, it may be reasonable to assume that the photochemical dissociation of X to XII and bromine results from a *n*-π^* triplet state of X.

There is another question concerning how the intermediary phenoxyl XII, which is known to be very stable in the dark, abstracts a hydrogen to afford XIII. Irradiation of the solution of the phenoxyl XII in benzene and petroleum ether with a high-pressure mercury arc lamp through a pyrex filter under bubbling nitrogen gave XIII in 47 and 71% yields, respectively. The photochemical disappearance of the phenoxyl XII in various solvents was followed by the decrease of the ultraviolet maximum at 630 mμ. The result shown in Fig. 2 indicates that the reaction rate of XII increases in the order: benzene, *N*,*N*-dimethylformamide and *n*-hexane. Analogous phenomena have been observed in the photolysis of a stable radical, diphenylpicrylhydrazyl (DPPH), in various solvents. Pitts *et al.*,[9] reported that hydrogen abstraction of DPPH afforded diphenylpicrylhydrazine. The ultraviolet spectrum of the phenoxyl XII showed a maximum at 625 mμ and a minimum at 450 mμ in benzene. A light at 625±7 mμ did not accelerate the hydrogen-abstraction of XII, but that at shorter wavelengths than 450 mμ did.*2

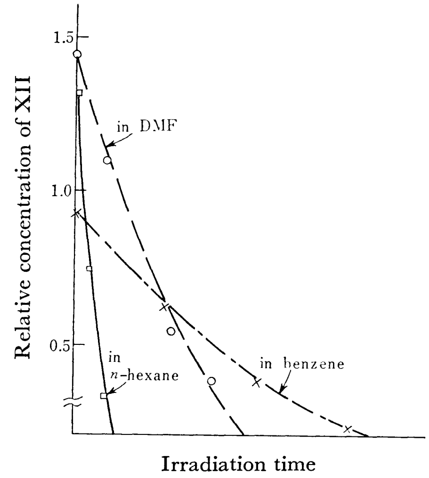

Fig. 2

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*1 A kinetic consideration supports the conclusion that XII reacts with a bromine molecule. The mechanism shown in the following scheme is adequate to describe the disappearance of XII which was formed by irradiation of X in *N*,*N*-dimethylformamide.

$$\mathrm{XII} + \mathrm{Br_2} \xrightarrow{k_1} \mathrm{X} + \mathrm{Br} \qquad (1)$$

$$\mathrm{XII} + \mathrm{Br} \xrightarrow{k_2} \mathrm{X} \qquad (2)$$

$$\mathrm{XII} \xrightarrow{k_3} \text{products} \qquad (3)$$

$$2\mathrm{Br} \xrightarrow{k_4} \mathrm{Br_2} \qquad (4)$$

where, k_1 and k_2 are the rate constants for reactions (1) and (2), and k_3 for the first-order decomposition of XII (3). The disappearance of XII follows the next equation.

$$-\frac{d[\mathrm{XII}]}{dt} = k_1[\mathrm{XII}][\mathrm{Br_2}] + k_2[\mathrm{XII}][\mathrm{Br}] + k_3[\mathrm{XII}]$$

In the early stages, it is inferred that $1/2[\mathrm{XII}]=[\mathrm{Br_2}]$ and the fourth equation was neglected ($k_2[\mathrm{Br}]=k_1[\mathrm{Br_2}]$). In this case, the above-mentioned equation may be written as

$$-\frac{d[\mathrm{XII}]}{dt} = k_1[\mathrm{XII}]^2 + k_3[\mathrm{XII}]$$

Integration of this equation gives the equivalent expression

$$\log\frac{[\mathrm{XIII}]_0}{[\mathrm{XII}]_0+k_3/k_1} - \log\frac{[\mathrm{XII}]}{[\mathrm{XII}]+k_3/k_1} = k_3t$$

where $[\mathrm{XII}]_0$=the concentration of XII at time $t=0$. Supposing that k_3/k_1 is 0.05, a plot of log (XII/XII+k_3/k_1) against time is linear in the early stage (Fig. 1).

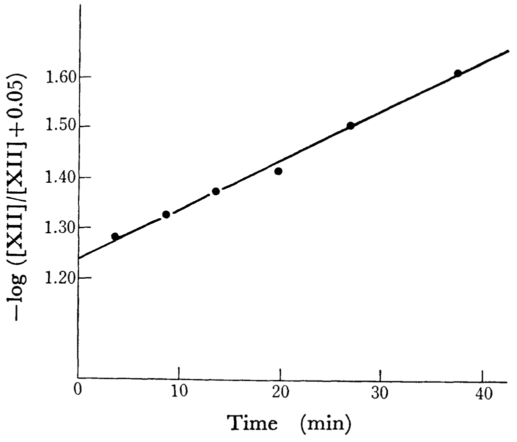


Fig. 1

This indicates that the disappearance of the phenoxyl XII may be largely attributed to its reaction with bromine molecules.

[8] T. Matsuura, This Bulletin, **37**, 564 (1964).

[9] J. N. Pitts, Jr., E. A. Schuck and J. K. S. Wan, *J. Amer. Chem. Soc.*, **86**, 296 (1964).

*2 The selected light was obtained by a concave radiation monochromator (Japan Spectroscopic Co., Model CRM-50). For its performances see Ref. 10.

[10] a) T. Matsuura and K. Ogura, *ibid.*, **89**, 3846 (1967); b) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, **1966**, 423.

When a solution of 2,4,6-tri-*t*-butyl-4-nitro-2,5-cyclohexadienone (XI) in benzene was irradiated with a 450-W high-pressure mercury arc lamp (Pyrex filter) under bubbling nitrogen, the reaction mixture, was shown to contain 2,4,6-tri-*t*-butylphenol (XIII, 6%), 2,6-di-*t*-butyl-*p*-benzoquinone (XV, 11%) and 2,4,6-tri-*t*-butyl-4-hydroxy-2,5-cyclohexadienone (XX, trace). Irradiation ($>$318 mμ) of XI in petroleum ether yielded XV (17%), XX (10%) and 3,5-di-*t*-butyl-*o*-benzoquinone (XXI, 5%) along with a trace of XIII. On the other hand, XIII was formed as the main product of the photolysis of XI in polar solvents such as *N*,*N*-dimethylformamide (28%) and methanol (43%). The results are summarized in Table 3.

TABLE 3. PHOTOLYSIS OF XI

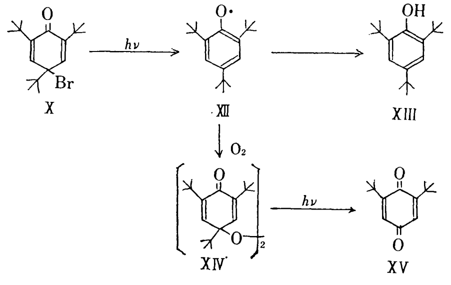
Solvent	Yield (%)[c] XIII	Yield (%)[c] XV
DMF[a]	28	—
Methanol[a]	35 (43)	—
Ether[b]	(8)	(11)
Benzene[a]	11 (6)	(11)
Petroleum ether[b]	trace	(17)

a) $>$280 mμ (Pyrex filter)

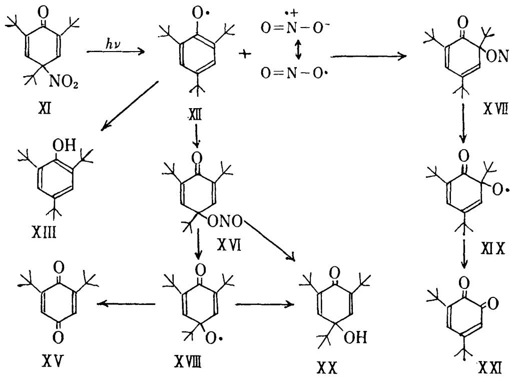
b) $>$318 mμ (through a 0.08 M solution of naphthalene in benzene)

c) Yields in parenthesis were obtained by VPC analysis.

The formation processes of these products may be rationalized as shown in Scheme II. In the first step, XI suffers homolytic decomposition to give XII and nitrogen dioxide, which has two resonance structures, O-radical and N-radical forms. The recombination of the radical XII and nitrogen dioxide (as the O-radical form) produces two isomeric nitrites (XVI and XVII). These nitrites undergo further photochemical cleavage of O–NO bond give XVIII and XIX, which are de-*t*-butylated to the corresponding benzoquinones, XV and XXI, respectively. The compound XX may be formed by hydrogen abstraction of XVIII or by hydrolysis of XVI during working up. Since XII and bromine recombine slowly in polar solvents, as mentioned already, it is expected that the recombination of XII and nitrogen dioxide is also a slow process. In fact, XIII was a major product in photolysis of XI in methanol and *N*,*N*-dimethylformamide, but XV could not be detected. Furthermore, it may be reasonable that the recombination of XII and nitrogen dioxide is a faster process in non-polar solvents, and that the formation of XV is predominant over the hydrogen abstraction of XII to afford XIII.



Scheme I



Scheme II

Experimental

Reaction of X in the Dark. Bromodienone X[6] was very unstable on silica gel and neutral alumina, but considerably stable in refluxed benzene. A solution of X (400 mg) in 10 m*l* petroleum ether was adsorbed on 20 g of silica gel and then allowed for half an hour at room temperature. Elution with 50 ml of petroleum ether gave 179 mg (56%) of colorless crystals which were identified as 2,4-di-*t*-butyl-6-bromophenol[6] (by IR). Further elution with 150 m*l* of petroleum ether afforded 110 mg (36%) of colorless crystals which were identified as 2,4,6-tri-*t*-butylphenol (XIII) (by IR). Elution with 50 m*l* of benzene yielded 3 mg of a yellow oil which was not further investigated. Continuous elution with 50 m*l* of benzene gave 28 mg (11%) of orange crystals which were identified as 2,6-di-*t*-butyl-*p*-benzoquinone (XV)[11] (by IR). The results were reproducible.

After X (300 mg) was adsorbed on 30 g of neutralized alumina (Woelm Co., Act. I), elution with 200 m*l* of petroleum ether and 100 m*l* of benzene gave 8 mg of a yellow oil which was not further investigated. Further elution with 150 m*l* of chloroform afforded 199 mg (83%) of pale yellow crystals which were identified as 2,4,6-tri-*t*-butyl-4-hydroxy-2,5-cyclohexadienone (XX)[11] (by IR).

A solution containing 200 mg of X in 20 m*l* of benzene was refluxed for 6 hr. The reaction mixture was evaporated under reduced pressure to yield pale yellow crystals which exhibited the same IR spectrum as that of X and were shown by TLC analysis not to contain

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[11] E. Müller and K. Ley, *Chem. Ber.*, **88**, 601 (1955).

2,4-di-*t*-butyl-6-bromophenol.

Photolysis of X. Since the starting material X was very unstable on silica gel and had a similar retention time on VPC to that of XIII to make VPC analysis difficult, the yield of the recovered X was estimated from the amount of 2,4-di-*t*-butyl-6-bromophenol which could be shown by TLC analysis not to exist in the photolysis mixture of X and which might be derived from the decomposition of X on silica gel.

a) In n-Hexane for a Long Period of Time under Bubbling Nitrogen. A solution containing 500 mg of X in 60 m*l* of *n*-hexane was irradiated for 45 min with a 100-W high-pressure mercury arc lamp surrounded by a Pyrex jacket under bubbling nitrogen. After addition of *n*-hexane (100 m*l*), the reaction mixture was washed with water and evaporated under reduced pressure. The residue was chromatographed on 20 g of silica gel. Elution with 200 m*l* of petroleum ether gave 309 mg (81%) of colorless crystals which were identified as XIII (by IR). In another run, VPC analysis of the reaction mixture (silicon DC 550, 1.5 m; 180°C; carrier gas: H_2, 1.5 kg/cm^2) showed that the yield of XIII was 81%.

b) In n-Hexane for a Short Period of Time under Bubbling Nitrogen. A solution containing 500 mg of X in 60 m*l* of *n*-hexane was irradiated for 13 min under the same conditions as described above. After evaporation of the solvent under reduced pressure, the residue was chromatographed on 20 g of silica gel. Elution with 50 m*l* of petroleum ether gave 41 mg of colorless crystals which were identified as 2,4-di-*t*-butyl-6-bromophenol (by IR). Further elution with 50 m*l* of petroleum ether afforded 153 mg of colorless crystals which were shown by IR analysis to consist of 101 mg of 2,4-di-*t*-butyl-6-bromophenol and 52 mg of XIII. Elution with 250 m*l* of petroleum ether yielded 134 mg of colorless crystals which were identified as XIII (by IR). Elution with 100 m*l* of benzene - petroleum ether (1 : 1) gave 20 mg of a yellow oil which was not further investigated. Continuous elution with 100 m*l* of benzene afforded 27 mg of orange crystals which were identified as XV. The yields of X, XIII and XV were 63, 27 and 2%, respectively.

c) In n-Hexane under Bubbling Oxygen. A solution containing 500 mg of X in 60 m*l* of *n*-hexane was irradiated for 14 min with a 100-W high-pressure mercury arc lamp (Pyrex filter) under bubbling oxygen. After evaporation of the solvent under reduced pressure, the residue was chromatographed on 20 g of silica gel. Elution with 300 m*l* of petroleum ether gave 12 mg of a colorless oil which was not further investigated. Further elution with 150 m*l* of benzene afforded 179 mg (56%) of orange crystals which were identified as XV (by IR).

d) In Benzene. A solution containing 2.00 g of X in 70 m*l* of benzene was irradiated for 6.75 hr under the same conditions mentioned in a). After removal of the solvent under reduced pressure, the residue was shown by VPC analysis to contain XIII and bromobenzene in 56 and 4.5% yields, respectively.

e) In Ether. A solution containing 500 mg of X in 60 m*l* of ether was irradiated under the same conditions described in a). The reaction mixture was evaporated under reduced pressure and the residue was shown by VPC analysis to contain XIII in a 88% yield.

f) In N,N-Dimethylformamide for a Long Period of Time. A solution containing 500 mg of X in 60 m*l* of *N,N*-dimethylformamide was photolyzed for 62 min under the same conditions mentioned in a). After addition of 200 m*l* of water, the reaction mixture was extracted with three 100-m*l* portions of ether. The ethereal layer was washed with water and dried on anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was shown by VPC analysis to contain XIII and XV in 56 and 7% yields, respectively.

g) In N,N-Dimethylformamide for a Short Period of Time. A solution containing 500 mg of X in 60 m*l* of *N,N*-dimethylformamide was irradiated for 15 min under the same conditions described in a). The resulting blue solution was allowed to stand for 2 hr under bubbling nitrogen to give a yellow solution. After addition of 150 m*l* of ether, the reaction mixture was washed with water and dried on anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the residue, which was shown by TLC analysis not to contain 2,4-di-*t*-butyl-6-bromophenol, was chromatographed on 20 g of silica gel. Elution with 50 m*l* of petroleum ether gave 144 mg of colorless crystals which were identified as 2,4-di-*t*-butyl-6-bromophenol (by IR). Further elution with 50 m*l* of petroleum ether afforded 94 mg of colorless crystals which were shown by IR analysis to consist of 32 mg of 2,4-di-*t*-butyl-6-bromophenol and 62 mg of XIII. Elution with 250 m*l* of petroleum ether yielded 91 mg of colorless crystals which were identified as XIII (by IR). Elution with 200 m*l* of benzene - petroleum ether (1 : 1) gave 5 mg of a yellow oil which was not further investigated. The continuous elution with 100 m*l* of benzene - petroleum ether (1 : 1) afforded 25 mg of orange crystals which were identified as XV (by IR). The yields of X and XIII were 77 and 14%, respectively.

h) In N,N-Dimethylformamide under Bubbling Oxygen. A solution containing 500 mg of X in 60 m*l* of *N,N*-dimethylformamide was irradiated for 15 min under the same conditions mentioned in c). After addition of ether (150 m*l*), the mixture was washed with water and dried on anhydrous sodium sulfate. The ethereal solution was evaporated under reduced pressure and the residue, which was shown by TLC analysis not to contain 2,4-di-*t*-butyl-6-bromophenol, was chromatographed on 20 g of silica gel. Elution with 50 m*l* of petroleum ether gave 134 mg of colorless crystals which were identified as 2,4-di-*t*-butyl-6-bromophenol (by IR). Further elution with 200 m*l* of petroleum ether afforded 84 mg of colorless crystals which were identified as XIII (by IR). Elution with 50 m*l* of benzene - petroleum ether (1 : 1) yielded 10 mg of a yellow oil which was not further investigated. Continuous elution with 130 m*l* of benzene - petroleum ether (1 : 1) gave 62 mg of orange crystals which were identified as XV (by IR). The yields of X and XV were estimated to be 59 and 13%, respectively. In another run, the photolyzed mixture was shown by VPC analysis to contain X and XV in 68 and 24% yields, respectively.

i) In Dimethyl Sulfoxide. A solution containing 500 mg of X in 60 m*l* of dimethyl sulfoxide and 10 m*l* of benzene was irradiated for 30 min under the same conditions described in a). During photolysis, the solution did not show a blue color, but a deep yellow. After addition of ether (100 m*l*), the reaction mixture was washed with water and dried on anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave a yellow oil which was shown by IR and TLC analyses to contain mainly X. The oil was chromatographed on 20 g of silica gel. Elution with 150 m*l* of petroleum ether afforded 175 mg of pale yellow crystals which were identified as 2,4-di-*t*-butyl-6-bromophenol (by IR). Further elution with 150 m*l* of petroleum ether yielded 94 mg of colorless crystals, which were identified as XIII (by IR). Elution with 100 m*l* of benzene - petroleum ether (1 : 1) gave 10 mg of a yellow oil which was not further investigated. Continuous elution with 200 m*l* of benzene - petroleum ether (1 : 1) afforded 67 mg of orange crystals which were identified as XV (by IR). It was estimated from these results that the yields of X and XV were 77 and 10%, respectively.

j) In Acetic Acid. A solution containing 500 mg of X in 100 m*l* of acetic acid was irradiated for 1 hr under the same conditions mentioned in a). After addition of ether (200 m*l*), the reaction mixture was washed with water and an aqueous bicarbonate solution and dried on anhydrous sodium sulfate. Evaporation of the solvent afforded a yellow oil which was chromatographed on 20 g of silica gel. Elution with 50 m*l* of petroleum ether gave 120 mg of colorless crystals which were identified as 2,4-di-*t*-butyl-6-bromophenol (by IR). Further elution with 150 m*l* of petroleum ether yielded 128 mg of colorless crystals which were identified as XIII (by IR). Elution with 100 m*l* of petroleum ether and 70 m*l* of benzene afforded 30 mg of a pale yellow oil which was not further investigated. Elution with 50 m*l* of benzene gave 33 mg of orange crystals which were identified as XV (by IR). The estimated yields of X, XIII and XV were 53, 15 and 5%, respectively.

Photolysis of the Phenoxyl Radical XII. *a) In Petroleum Ether.* A solution of the phenoxy radical XII in 400 m*l* of petroleum ether, prepared from 4.00 g of 2,4,6-tri-*t*-butylphenol (XIII) according to the known method,[12] was irrradiated with a 450-W high-pressure mercury arc lamp surrounded by a Pyrex water-cooled jacket under bubbling nitrogen until the blue color of the solution disappeared (irradiation time: 15 hr). The reaction mixture was evaporated under reduced pressure and the residue was shown by VPC analysis to contain XIII and XV in 71 and 13% yields, respectively. Eight-ninths of the reaction mixture was chromatographed on 50 g of silica gel. Elution with 200 m*l* of petroleum ether gave 1.90 g of pale yellow crystals which were identified as XIII (by IR).

b) In Benzene. A solution of XII in 400 m*l* of benzene, prepared from 4.00 g of XIII, was irradiated for 43 hr under similar conditions to those described in a) to afford a yellow solution. The reaction mixture was shown by VPC analysis to contain XIII and XV in 47 and 7%, respectively. The mixture was evaporated under reduced pressure to give a brown oil which, by crystallization from methanol, yielded 155 mg of pale yellow crystals, identified as XIII (by IR and mixture mp).

c) With a Selected Light. The selected light was obtained by a concave radiating monochromator (Japan Spectroscopic Co., Model CRM-50).[8] A solution of XII was prepared from 150 mg of XIII in 50 m*l* of benzene, which was treated with 1.30 g of lead dioxide followed by filtration of the reaction mixture under nitrogen atmosphere.[6] Each 4 m*l* of the solution was placed in a quartz cell (1 cm square) and irradiated with the selected light. The solution completely absorbed the incident light of wavelengths longer than 570 mμ and shorter than 410 mμ. The progress of the reaction was followed by decrease of the absorbances at 550 and 530 mμ. The relative rates of disappearance of XII with various wavelength lights were 1.0 at 305±7 mμ, 0.6 at 341±7 mμ, 0.6 at 377±7 mμ, 0.3 at 413±7 mμ, 0.2 at 449±7 mμ, 0.0 at 485±7 mμ, and 0.0 at 625±7 mμ.

Photolysis of XI. *a) In Methanol.* A solution containing 1.00 g of XI in 60 m*l* of methanol was irradiated for 1.5 hr with a 100-W high-pressure mercury arc lamp through a Pyrex filter under bubbling nitrogen. Evaporation of the solvent under reduced pressure gave a brown oil which was chromatographed on 20 g of silica gel. Elution with 410 m*l* of petroleum ether afforded 310 mg (35%) of colorless crystals which were identified as XIII (by IR).

A solution containing 500 mg of XI in 60 m*l* of methanol was also irradiated for 52 min under the same conditions as described above. The reaction mixture was shown by VPC analysis (Silicon DC 550, 1.5 m, 170°C. carrier gas: H_2, 1.5 kg/cm^2) to contain XIII in 43%.

b) In N,N-Dimethylformamide. A solution containing 500 mg of XI in 60 m*l* of *N,N*-dimethylformamide was irradiated for 45 min under the same conditions mentioned in a). After addition of ether (150 m*l*), the reaction mixture was washed with water and dried on anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure afforded a brown oil which was chromatographed on 20 g of silica gel. Elution with 130 m*l* of petroleum ether gave 121 mg (28%) of colorless crystals which were identified as XIII (by IR).

c) In Ether. A solution containing 1.00 g of XI in 400 m*l* of ether was irradiated for 4 hr and 11 min with a 100-W high-pressure mercury arc lamp under bubbling nitrogen through the filter solution, which contained 1 g of naphthalene in 100 m*l* of benzene and absorbed completely the incident light of wavelength shorter than 318 mμ. The reaction mixture was shown by VPC analysis to contain XV in 11%. Three-fourths of the reaction mixture was evaporated under reduced pressure and chromatographed on 20 g of silica gel. Elution with 30 m*l* of benzene - petroleum ether (1 : 1) yielded 53 mg of pale yellow crystals which were identified as XIII (by IR).

d) In Benzene. A solution containing 500 mg of XI in 60 m*l* of benzene was irradiated for 52 min under the same conditions described in a). The reaction mixture was shown by VPC analysis to contain XIII and XV in 6 and 11%, respectively. A solution containing 2.00 g XI in 60 m*l* of benzene was also photolyzed for 5.5 hr under the same conditions mentioned above. After removal of the solvent under reduced pressure, the residue was chromatographed on 60 g of silica gel. Elution with 25 m*l* of benzene - petroleum ether (1 : 1) gave 188 mg of pale yellow crystals which was shown by IR analysis to consist mainly of XIII. Further elution with 365 m*l* of benzene- petroleum ether afforded 350 mg of a brown oil which was not further investigated. Elution with 100 m*l* of the same solvent yielded 89 mg of orange crystals which were identified

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12) E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

as XV (by IR). Elution with 350 m*l* of petroleum ether-benzene gave 190 mg of a orange oil which was not further investigated. Continuous elution with 150 m*l* of benzene afforded 46 mg of a pale yellow oil containing a small amount of colorless crystals (8 mg), which were separated by filtration and identified as XX (by IR).

e) In Petroleum Ether. A solution containing 1.00 g of XI in 400 m*l* of petroleum ether was irradiated for 3.5 hr under the same conditions as described in c). The reaction mixture was shown by VPC analysis to contain XV in 17%. Three-fourths of the reaction mixture was evaporated under reduced pressure and chromatographed on 30 g of silica gel. Elution with 500 m*l* of petroleum ether gave 29 mg of a yellow oil which was shown by TLC analysis to contain a trace of XIII. Further elution with 130 m*l* of petroleum ether - benzene (1 : 1) afforded 88 mg of a yellow oil which was not further investigated. Elution with 100 m*l* of petroleum ether - benzene (1 : 1) yielded 95 mg of orange crystals which were identified as XV (by IR). Elution with 150 m*l* of the same solvent gave 71 mg of pale yellow crystals which were identified as XX (by IR). Elution with 430 m*l* of benzene afforded 114 mg of a brown oil which was not further investigated. Continuous elution with 300 m*l* of benzene and with 100 m*l* of methylene chloride yielded 99 mg of purple crystals which were further purified by preparative TLC to give 27 mg of XXI(13) (identified by IR).

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13) W. Flay, T. Ploetz and H. Biergans, *Ann. Chem.*, **597**, 196 (1955).