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PHOTOINDUCED REACTIONS—XXXVII

PHOTOCHEMICAL REACTION OF 2,4,6-TRI-*t*-BUTYL-3-METHOXY-2,5-CYCLOHEXADIENONE[1]

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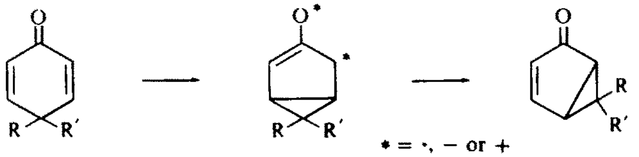
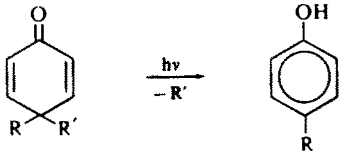
Abstract—Irradiation of 2,4,6-tri-t-butyl-3-methoxy-2,5-cyclohexadienone (III) in benzene afforded 3,6-di-t-butylguaiacol (II) and a benzocyclobutene (V) in high yields. The ratio of II to V depends on the wavelength of the incident light and decreases on irradiation with light of shorter wavelengths. Furthermore, V was formed the faster in the order of the wavelengths of the incident light: 361 ± 7, 325 ± 7, and 289 ± 7 mμ. These facts indicate that the m,π* excitation of III is mainly responsible for the formation of II and the π,π* excitation predominantly for the formation of V. Possible explanations for these phenomena are discussed.

THE photochemical reaction of 2,5-cyclohexadienones has been shown to result in the formation of several types of products. Isomerization to a bicyclo[3.1.0]hex-3-en-2-one, the so-called lumi-type ketone, is the most common process (Eq. 1).[2] It was also reported that some of 2,5-cyclohexadienones caused photochemically expulsion of one of the 4-substituents followed by phenol formation (Eq. 2).[2,3]



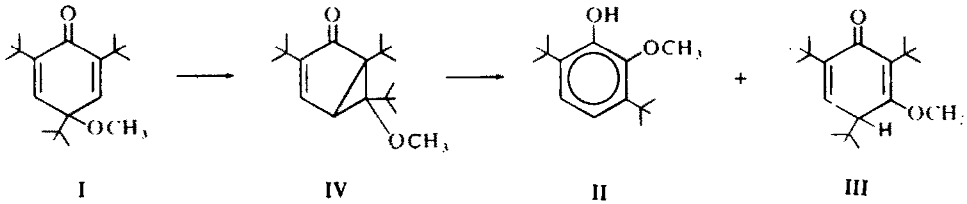
(Eq. 1)



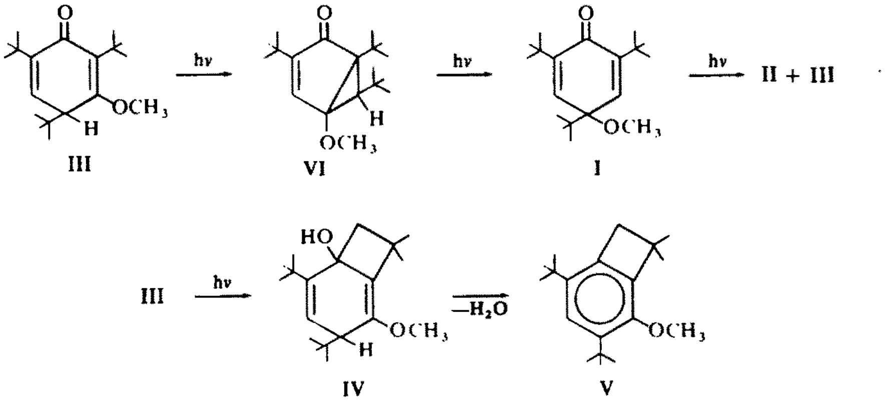
(Eq. 2)

In a previous paper,[4] we reported that irradiation of 2,4,6-tri-t-butyl-4-methoxy-2,5-cyclohexadienone (I) suffered a similar transformation to the usual cross-conjugated cyclohexadienone to yield a photophenol (II) and a photoketone (III) which underwent further conversion on irradiation for a longer period of time (Scheme 1). We now wish to report the photo-chemical reaction of photoketone III, a 2,5-cyclohexadienone containing a OMe group at C-3 position, which gave the photophenol II produced *via* a lumi-type ketone (IV) and a benzocyclobutene (V) formed *via* a cyclobutanol (VI) (Scheme 2). The formation of the cyclobutanol VI is the first example of the photochemical intramolecular hydrogen abstraction by the carbonyl group of a 2,5-cyclohexadienone.

SCHEME 1



SCHEME 2



RESULTS AND DISCUSSION

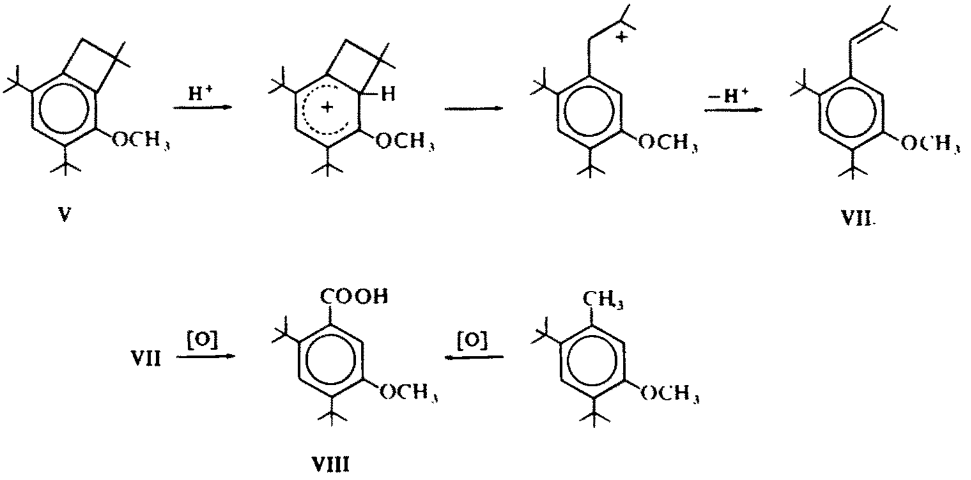
Photolysis of III

Irradiation of the photoketone III in benzene with a high-pressure Hg arc lamp filtered through Pyrex yielded the photophenol II (25%) and the benzocyclobutene V (38%) along with a small amount of the starting material (7%). The benzocyclobutene V was also obtained on irradiation of III in methanol (10%) with a high-pressure Hg lamp and in ether (11%) or n-hexane (12%) with a low-pressure Hg lamp. Distribution of the products is not reproducible but depends on the wavelength of the incident light as described below.

Molecular formula $C_{19}H_{30}O$ for the benzocyclobutene V was confirmed by its mass spectrum and the elementary analysis. The IR bands at 1603, 1575 and 1485 cm^{-1} and the UV maxima at 275 (ε 890) and 270 mμ (ε 904) indicate that V has a benzene ring. The NMR spectrum of V shows six singlets at τ 3·06 (1H, an aromatic proton), 6·17 (3H, a OMe group on a benzene ring), 7·07 (2H, a methylene group), 8·48 (6H, two equivalent Me groups), 8·69 (9H, a t-Bu) and 8·75 (9H, a t-Bu). It is deduced from the above-mentioned data that V is a benzocyclobutene with two Me groups on one C atom of the cyclobutene ring and two t-Bu groups and a OMe group on the benzene ring. Treatment of V with hydrochloric acid in acetic acid at 50° gave a styrene derivative (VII). The NMR and UV spectra suggest that it is a β,β-dimethylstyrene derivative. The UV bands of VII at 241 (ε 7700) and 279 mμ (ε 2200) are similar to those of 3-methoxystyrene [250 (ε 8500) and 293 mμ (ε 2150)][5] and the NMR spectrum of VII indicates the presence of 2,2-dimethylvinyl group [τ 3·52 (1H, diffused s), 8·12 (3H, d, J = 1·5 c/s) and 8·41 (3H, d, J = 1·5 c/s)], two t-Bu groups (τ 8·66 and 8·70), a OMe group (τ 6·24) and two aromatic protons [τ 2·85 (1H, s) and 3·62 (1H, s)]. Permanganate oxidation of VII yielded an acid (VIII), which showed IR bands at 3600 ~ 2400 cm^{-1} and 1700 cm^{-1} and UV maxima at 230 mμ (ε 7100) and 281 mμ (ε 2250) characteristic of a benzoic acid derivative.* In the NMR spectrum of VIII, six singlets appeared at τ −1·82 (1H, COOH), 2·53 (1H, an aromatic proton), 2·95 (1H, an aromatic proton), 6·13 (3H, a OMe group on benzene ring), 8·52 (9H, t-Bu) and 8·60 (9H, t-Bu). Structure VIII was assigned for the acid from the spectral properties. This was confirmed by an unambiguous synthesis of VIII, i.e. permanganate oxidation of 2,4-di-t-butyl-5-methylanisole.[7]

Accordingly, formulas VII and V were given as the structures of the styrene derivative and the benzocyclobutene, respectively. The acid-catalyzed rearrangement of V to VII may be explained as shown in Scheme 3.

SCHEME 3



Mechanistic consideration

The formation of the photophenol II from the photoketone III can be rationalized as the usual photochemical reaction of 2,5-cyclohexadienones.[2] In the first step photoketone III isomerizes photochemically to the lumi-type ketone IV. Next IV undergoes photochemical t-Bu migration to form the cyclohexadienone I which is further converted to the photophenol II and the starting material III as reported.[4] In fact, the presence of the I as an intermediate was confirmed by following the reaction as a function of time by VPC analysis (Fig. 1). The photochemical process from III to I is quite analogous to that from I to III. Although the formation of an isomeric

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* The UV spectrum of benzoic acid shows the maxima at 228 (ε 10,000) and 279 mμ (ε 550).[6]

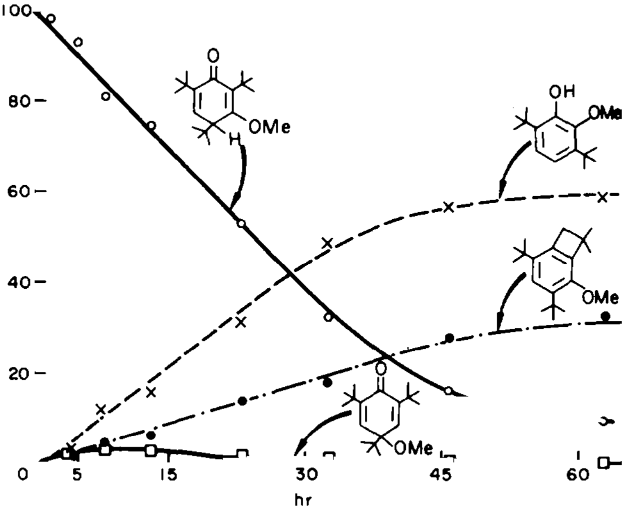
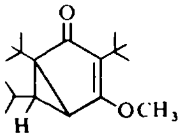
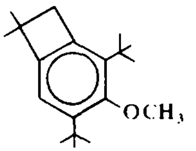


FIG. 1

lumi-type ketone IX from III is possible for an alternative course, we could not detect IX and any other products possibly derived from IX in the reaction mixture. However, we cannot distinguish between two possibilities; (i) the formation of IV from III may greatly predominate over the formation of IX and (ii) IX may revert photochemically to III even though IX is first produced.



IX



X

It is reasonable that the benzocyclobutene V is formed *via* the cyclobutanol VI which is produced by hydrogen abstraction by the excited CO group of III. It is known that a ketone with an H atom in the γ-position gives photochemically a cyclobutanol,[8] and that cyclobutanol formation becomes easier as an H atom is sterically more close to the O atom of the ketone.[9] It is reasonable that hydrogen abstraction from the t-Bu group at C-2 occurs predominantly because this t-Bu group is to the CO group than the t-Bu at C-6 position by steric repulsion with the OMe group at C-3 position.

It should be noted that the ratio of the benzocyclobutene V to the photophenol II increases by irradiation with the incident light of shorter wavelengths as shown in Table 1 and that the benzocyclobutene was formed faster as the wavelength of the incident light became shorter (Table 2). These facts and the n,π* absorption of III (Fig. 2) suggest that the n,π* excitation is responsible mainly for the rearrangement of III to the lumiketone IV, and that the π,π* excitation by the light of higher energy

TABLE 1. WAVELENGTH DEPENDENCY OF THE PHOTOCHEMICAL REACTION OF III[a]

Additive	Filter[b]	Product distribution (%)			Irrad time (hr)
		II	V	III	
None	A	11	8	81	19
None	B	5	20	75	19
Acetophenone (5·5 g)	B	2	11	35	9

[a] A solution of 150 mg of III in 400 ml of benzene was used.

[b] A = the solution containing 0·05M naphthalene in benzene (>318 mμ). B = benzene (>280 mμ).

TABLE 2. IRRADIATION OF III WITH THE SELECTED LIGHT[a,b]

Wavelength (mμ) of the incident light	Relative intensity of light	Yield (%)[c] of V	Relative rate of formation of V
289 ± 7	16·3	3·9	3·0
325 ± 7	19·1	2·5	1·6
361 ± 7	17·6	1·4	1·0

[a] The selected light was obtained by a concave radiating monochromator (Japan Spectroscopic Co., Model CRM-50).[10]

[b] A 0·0067M solution of III in cyclohexane.

[c] Conversion of III: 4–5%.

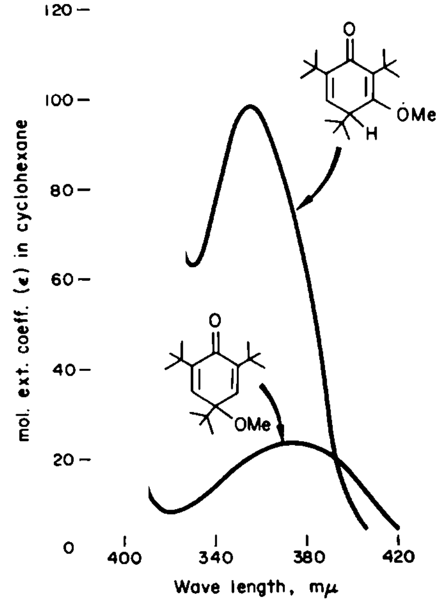
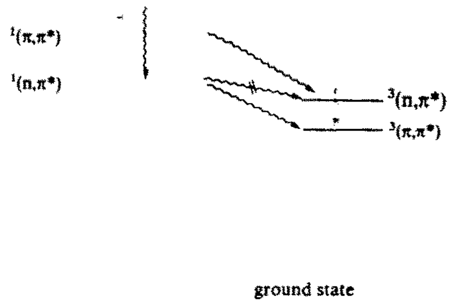


FIG. 2

leads predominantly to the benzocyclobutene V. Furthermore, it was shown by the sensitized reaction (Table 1) that the benzocyclobutene V is formed *via* the triplet excited state of the photoketone III. This accords with the fact that cyclobutanol formation in photolysis of 2-pentanone or 2-hexanone arises exclusively from their triplet states.[11] These facts indicate that the formation of the benzocyclobutene V occurs from a higher triplet state.

We now wish to discuss possible explanations for the photochemical reaction of III. First, it is possible that the isomerization of the photoketone III to IV occurs from the $^3(n,\pi^*)$ state, and that the formation of the benzocyclobutene V arises from a higher triplet state, i.e. $^3(\pi,\pi^*)$ state. Second, the wavelength-dependency of the photochemical reaction of III can be rationalized by assuming that IV and V are formed from $^3(\pi,\pi^*)$ state and $^3(n,\pi^*)$ state with a higher energy, respectively. It is generally accepted that hydrogen abstraction of a CO group involves $^3(n,\pi^*)$ state as a reactive species but not $^3(\pi,\pi^*)$ state.[12] Zimmermann suggested by configuration interaction (CI) calculation that the rearrangement of a 2,5-cyclohexadienone to a lumiketone is initiated from $^3(n,\pi^*)$ state because bonding between C-3 and C-5 is unlikely in $^3(\pi,\pi^*)$ state.[13] Therefore, two explanations mentioned above seem improbable.

SCHEME 3



Supposing the energy of $^3(\pi,\pi^*)$ level of III is lower than that of $^3(n,\pi^*)$ level as shown in Scheme 3,† excitation to the $^1(\pi,\pi^*)$ state of III may be followed by intersystem-crossing to $^3(n,\pi^*)$ state and by internal conversion to $^1(n,\pi^*)$ state, the molecule in the $^1(n,\pi^*)$ state may not be led to the $^3(n,\pi^*)$ state but to the $^3(\pi,\pi^*)$ state by the intersystem-crossing.‡ This supposition may enable the third explanation that the molecule in the $^3(n,\pi^*)$ state, which is produced exclusively from $^1(\pi,\pi^*)$ excitation of III,

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† Usually the n,π* portions of the UV absorption and of the emission spectrum shift to shorter wavelength by introduction of the electron-releasing groups, and the reverse is found for the π,π* portions. In case of the cross-conjugated cyclohexadienone, the energy difference between $^3(\pi,\pi^*)$ and $^3(n,\pi^*)$ configurations is so small (0·03 eV by CI calculation)[13] that introduction of a OMe group at C-3 position can make $^3(\pi,\pi^*)$ state lower than $^3(n,\pi^*)$ state. In fact, the n,π* absorption maximum of III was found at a shorter wavelength (356 mμ) than that of I (374 mμ) (Fig. 2).

‡ It is expected by the application of El-Sayed's theory[14] to the carbonyl compound that the transfer from $^1(n,\pi^*)$ state to $^3(\pi,\pi^*)$ state have a fairly high rate and the intersystem crossing from $^1(n,\pi^*)$ state to $^3(n,\pi^*)$ state may be slow. Since the $^1(\pi,\pi^*)$ configuration interacts strongly with $^3(n,\pi^*)$ configuration, the process from $^1(\pi,\pi^*)$ to $^3(n,\pi^*)$ may be allowed.[15]

is led mainly to the lumiketone V and, as a minor process, to IV which is also formed directly from the $^1(n,\pi^*)$ state.†

We can explain the low efficiency of the photochemical reaction of III (1/180 compared with that of the cyclohexadienone I by the above-mentioned energy relation which suggests that both of the reactive species[$^1(n,\pi^*)$ and $^3(n,\pi^*)$ state] is short-lived.

EXPERIMENTAL

Photolysis of the photoketone III

(a) *In benzene.* A soln containing 5·00 g of III in 1000 ml benzene was irradiated for 118 hr with a 450-W high-pressure Hg arc lamp (Ushio UM 450) surrounded by a Pyrex jacket under bubbling N_2. After removal of the solvent under reduced press, the residue was crystallized from MeOH to give 1·20 g of pale yellow crystals, m.p. 96–99°, which, by recrystallization from MeOH, afforded V as colourless needles, m.p. 99·5–100°; λ_{max}^{EtOH} 275 mμ (ε 890), 270 (ε 904) and 220 (shoulder, ε 11,300); NMR spectrum: τ^{CCl_4} 3·06 (1H, s), 6·17 (3H, s), 7·07 (2H, s), 8·48 (6H, s), 8·69 (9H, s) and 8·75 (9H, s); mass spectrum: *m/e* 274 (parent peak, relative intensity 0·30), 259 (base peak, 1·00), 57 (0·36) and 41 (0·18). (Found: C, 82·96; H, 11·12. Calc. for $C_{19}H_{30}O$: C, 83·15; H, 11·02%).

The mother liquor was evaporated and the residue was chromatographed on 50 g of silica gel. Elution with 450 ml light petroleum gave 1·46 g of a yellow oil (fraction A). Further elution with 200 ml light petroleum yielded 149 mg of pale yellow crystals, which were recrystallized from MeOH to afford 50 mg of colourless crystals, m.p. 83·5–84·5°, identified as II[4] (by IR and mixture m.p.). The mother liquor from II and the fraction A were combined and evaporated. The residue was shown by IR analysis to consist of II and V (3:2). Chromatography of the residue followed by further elution with 300 ml light petroleum and 100 ml benzene–light petroleum (1:9) yielded 334 mg (7%) of pale yellow crystals which were identified as the starting material (by IR). The total yields of II and V amounted to 25% and 39%, respectively.

(b) *In methanol.* A soln of 1·50 g of III in 450 ml MeOH was irradiated for 37 hr under the same conditions mentioned. The solvent was evaporated and the residue was chromatographed on 50 g of silica gel. Elution with 50 ml light petroleum–benzene (7:3) yielded 112 mg of colourless crystals, which were identified as V (by IR). Further elution with 100 ml light petroleum–benzene (7:3) gave 135 mg of yellow semi-crystals, which were recrystallized from MeOH to afford 27 mg of colourless crystals, identified as V (by IR). Elution with 70 ml light petroleum–benzene (7:3) yielded 99 mg of yellow crystals, which, by recrystallization from MeOH gave 26 mg of III (identified by IR).

(c) *In ether with a low-pressure mercury arc lamp.* A soln containing 500 mg of III in 250 ml ether was irradiated for 23·5 hr under bubbling N_2 using a 6-W low-pressure Hg arc lamp (Vycor filter) and cooled externally with water. After removal of the solvent, the residue was chromatographed on 20 g of silica gel. Elution with 150 ml light petroleum yielded 52 mg of colourless crystals, identified as V (by IR).

(d) *In* n-*hexane.* A soln of 200 mg of III in 230 ml n-hexane was irradiated for 14 hr under the conditions mentioned in (c). After evaporation of the solvent under reduced press, the residue was adsorbed on 5 g of silica gel. Elution with 50 ml of benzene gave 141 mg of a yellow oil, which was shown by VPC analysis [silicon DC 550 (1·5 m). Carrier gas H_2 (0·7 kg/cm^2). column temp: 210°] to contain 18 mg (11%) of V and 25 mg (13%) of III.

Acid treatment of the benzocyclobutene V

A soln containing 700 mg of V, 10 ml conc HCl in 40 ml AcOH was stirred at 50° for 2 hr. After addition of 100 ml water, the mixture was extracted with three 100-ml portions ether. The ethereal layer was washed with water and sat $NaHCO_3$ aq and then dried on Na_2SO_4. Removal of the solvent afforded a pale yellow oil which was chromatographed on 40 g of silica gel. Elution with light petroleum gave 325 mg colourless crystals, which were recrystallized from MeOH to yield VII, as colourless crystals, m.p. 47–48°: λ_{max}^{EtOH} 241 mμ (log ε 3·89) and 279 (3·34); NMR spectrum: τ^{CCl_4} 2·85 (1H, s), 3·52 (1H, a broad s), 3·62 (1H, s), 6·24

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† It seems possible that a 2,5-cyclohexadienone isomerizes to a lumi-type ketone (Eq. 1) from its $^1(n,\pi^*)$ state, whose 3,5-bond order, $P_{3,5}$, is positive enough to produce a bond between C-3 and C-5 position.[13] However, it has been reported that isomerization to a lumi-type ketone occurs only from $^3(n,\pi^*)$ state.[3b, 13, 16] This may be due to efficiency of the conversion $^1(n,\pi^*) \rightarrow {^3(\pi,\pi^*)} \rightarrow {^3(n,\pi^*)}$ and the long life-time of $^3(n,\pi^*)$ state.

(3H, s), 8·12 (3H, d, J = 1·5 c/s), 8·41 (3H, d, J = 1·5 c/s), 8·66 (9H, s) and 8·70 (9H, s). (Found: C, 83·42; H, 11·01. Calc. for $C_{19}H_{30}O$: C, 83·15; H, 11·02%).

Oxidation of the styrene derivative VII

A mixture containing 300 mg V, 3·00 g KOH and 3·00 g $KMnO_4$ in 30 ml pyridine–water (1:1) was refluxed for 3 hr. After further addition of 1·00 g $KMnO_4$, the reflux was continued for 3·5 hr. The reaction mixture was cooled and acidified with conc H_2SO_4. The deposited MnO_2 was reduced with $NaHSO_3$ and 100 ml water added. The mixture was extracted with three 100-ml portions ether and the ethereal layer was washed with water and dried on Na_2SO_4. Evaporation of the solvent gave 290 mg of a pale yellow oil which crystallized, and recrystallization from light petroleum yielded 40 mg of colourless crystals, m.p. 146–148°, identified as VIII (by IR and mixture m.p.), which was synthesized as described below.

Oxidation of 2,4-di-t-butyl-5-methylanisole

A soln containing 1·00 g 2,4-di-t-butylmethylanisole,[7] 3·00 g KOH and 2·5 g $KMnO_4$ in 32 ml pyridine–water (1:1) was refluxed for 2 hr. The excess of permanganate was decomposed with MeOH and the mixture was acidified with conc H_2SO_4. After the reduction of the deposited MnO_2 with $NaHSO_3$, 100 ml water was added and the soln was extracted with three 100-ml portions ether. The ethereal layer was extracted with two 50-ml portions 10% KOH. The aqueous layer was acidified with 2N H_2SO_4 and the deposited colourless crystals (273 mg) were collected. Recrystallization from light petroleum affords VIII as colourless crystals, m.p. 150·5–151°; λ_{max}^{EtOH} 230 mμ (log ε 3·85) and 281 (3·35); NMR spectrum: τ^{CDCl_3} −1·82 (1H, s), 2·53 (1H, s), 2·95 (1H, s), 6·13 (3H, s), 8·52 (9H, s) and 8·60 (9H, s). (Found: C, 72·48; H, 9·01. Calc. for $C_{16}H_{24}O_3$: C, 72·69; H, 9·15%).

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