PHOTO-INDUCED REACTIONS—XVII

A BICYCLO[3.1.0]HEX-3-EN-2-ONE INTERMEDIATE IN THE PHOTOAROMATIZATION OF 2,4,6-TRIALKYL-6-ACETOXY-2,4-CYCLOHEXADIENONE¹

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Abstract—Photolysis of 2,4,6-tri-t-butyl-6-acetoxy-2,4-cyclohexadienone (VIa) in benzene yielded a bicyclo[3.1.0]hexen-2-one VIII, a dienone IX, and a phenol X together with 2,4,6-tri-t-butylphenol. The bicyclohexenone VIII was shown to be an intermediate in the formation of the dienone IX. On the other hand, irradiation of 2,6-di-t-butyl-4-methyl-6-acetoxy-2,4-cyclohexadienone (VIb) afforded a dienone XI, two phenols XII and XIII, and a ketone XIV. The phenol XII and the dienone XI were not obtained by the photolysis of the ketone XIV which may be formed by a skeletal rearrangement of VIb. The results suggest that the photoaromatization of 2,4,6-trialkyl-6-acetoxy-2,4-cyclohexadienones of type VI may proceed via an intermediate of type VIII which may be formed from the dienone VI by acetoxyl migration concomitant with bond alternation. The dienones IX and XI provide the first example of the ortho-ketone tautomer of monohydric phenols.

THE photochemical reaction of 6,6-disubstituted 2,4-cyclohexadienones has been shown to result in the formation of several types of products.²⁻⁴ Ring fission to *cis*-dieneketene is the most common process (Eq. 1).^{2,3} In sharp contrast, irradiation of 2,4,6-trimethyl-6-acetoxy-2,4-cyclohexadienone (I) gives predominantly 2,4,6-trimethyl-3-acetoxyphenol (III) and mesitol as a minor product.³ Zwitterions IIa and



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IIb have been tentatively proposed by Barton and Quinkert as intermediates in the conversion of I to III (Eq. 2).³ The third type of rearrangement has been recently reported by Hart *et al.* who demonstrated that 2,3,4,5,6,6-hexamethyl-2,4-cyclo-hexadienone (IV) undergoes skeletal rearrangement to give a bicyclo[3.1.0]hexenone V (Eq. 3).⁴

We have investigated the photoaromatization of highly hindered 2,4,6-trialkyl-6acetoxy-2,4-cyclohexadienones VIa and VIb analogous to I and now report evidence which indicates that a bicyclo[3.1.0]hex-3-en-2-one VIII may be an intermediate in the photoaromatization of VI.

Synthesis of dienones VIa and VIb. Oxidation of 2,4,6-tri-t-butyl phenol with lead tetraacetate gave 2,4,6-tri-t-butyl-6-acetoxy-2,4-cyclohexadienone VIa (57%) and

| | IR (KBr, cm ⁻¹) | UV maxima (EtOH, mμ (ε)) | | NMR (τ) ^α | | |
|------|--------------------------------|-----------------------------|------------------------------|-----------------------------|------------------------------------|--------------------------|
| | | | н | н | OCOCH ₃ CH ₃ | I-C₄ H9 |
| VIa | 1747, 1681* | 309 (4200) | 3·20 df, 4·22 df | | 7.95 | 8.78, 8.87, 9.06 |
| VIIa | 1747, 1645 ⁴ | 243 (15700) | 3.57 se | | 7·95 | 8·79 ¹ , 9·05 |
| VIb | 1745, 1675 | 315 (3400), 373 (sh, 558) | 3·59 d*, 4·28 m | | 7·98 8·09 đi | 8-81, 9-06 |
| унь | 1750, 1643 ^j | | 3·52* | | 8-00 8-53 s | 8·80 ^r |
| vIII | 1752, 1705 | 269 (2200), 220 (4700) | 3·10 s | 5-51 s | 8-08 | 8·78 ⁷ , 8·88 |
| IX | 1760, 1666 [*] | 315 (4500), 370 (sh, 950) | 3·13 s | 7·14 s | 7.86 | 8·80 ^r , 9·03 |
| х | 3390, 1731 | 276 (2900) | 2·84 s, 3·64 s | | 7·69 | 8·68, 8·70 |
| XI | 1763, 1663 ¹ | 318 (3600), 376 (sh, 860) | 3·58 s | 7·21 g‴ | 7·88 8·29 d‴ | 8.83, 9.03 |
| XII | 3500, 1750 | 278 (2700) | 3·10 s | - | 7·79 8·04 s | 8·55, 8·64 |
| ХШ | 3340, 1731 | 273 (3200) | 3-06 s, 3·72 s | | 7·75 7·96 s | 8.67 |
| XIV | 1750, 1700 | 223 (5700), 265 (sh, 2000) | 3-24 d ⁱ | 7.86* | 7·99 8·61 s | 8·83, 8·94 |
| xv | 1704, 1682 | 212 (4200), 238 (sh, 3200) | 2·71 d ^ø , 7·66 d | | 8.58 s | 8·80 ¹ |
| XVI | 1715, 1685 | 223 (10400), 272 (sh, 722) | 2.85 d ^e , 7.10 m | | 8 80 d ³ | 8.80, 8.85 |

TABLE 1. SPECTRAL DATA FOR NEW COMPOUNDS

^a Peak multiplicities are represented by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^b 1650 (sh). ^c J = 2.5 c/s. ^d 1663 (sh). ^e 2 protons. ^f two t-Bu groups. ^g 1660 (sh). ^h J = 2 c/s. ⁱ J = 1.5 c/s. ^j 1664 (sh). ^k 1646 cm⁻¹ (sh). ⁱ neat film, 1685 (sh). ^m J = 1 c/s.ⁿ broad singlet. ^p J = 19 c/s. ^q J = 2.6 c/s. ⁱ J = 2.4 c/s. ⁱ J = 4.0 c/s.

2,4,6-tri-t-butyl-4-acetoxy-2,5-cyclohexadienone VIIa (26%). Oxidation of 2,6-di-tbutyl-*p*-cresol, yielded two cyclohexadienones, VIb and VIIb, in 23% and 31% yields, respectively. The structures of these products were based on the spectral data (Table 1) and by considering the analogous oxidation of phenols with lead tetraacetate.⁵



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Photolysis of VIa. Irradiation of VIa in benzene with a high-pressure mercury arc lamp (Pyrex filter) yielded a mixture of products from which 2,4,6-tri-t-butyl phenol (7%), an isomeric ketone VIII (23%), an isomeric dienone IX (12%), an acetoxyphenol X (13%), and the unreacted I (8%) were isolated by column chromatography on silica gel. Photolysis of VIa in petroleum ether gave a similar mixture of the products. The spectral data (Table 1) and the fact that acetylation of the acetoxyphenol X gave the diacetate of 4,6-di-t-butylresorcinol,⁶ supported structure X for the acetoxyphenol. The isomeric dienone IX was shown to have a 2,4-cyclohexadienone skeleton from its IR band at 1666 cm⁻¹ with a shoulder at 1646 cm⁻¹ (KBr) and its UV maximum at 315 mµ (ε 4500) with a shoulder at 370 mµ (ε 950). The NMR spectrum of IX showed five singlets at τ 3.13 (1H, an olefinic proton), 7.17 (1H, an aliphatic proton), 7.86 (3H, an acetoxy group), 8.80 (18H, two t-butyl groups) and 9.03 (9H, a t-butyl group). These spectral data indicate that IX is a 6-monosubstituted 2.4cyclohexadienone. The structure IX assigned to the dienone is supported by the fact that treatment of IX with acetic acid affords the acetoxyphenol X. It has been shown by Miller and Margulies⁷ that 6-t-butyl-2,4-cyclohexadienones decompose thermally or by mild acid treatment to give de-t-butylated phenols. The dienone IX provides the first example of the ortho-ketone tautomer of a monohydric phenol.[†]

The ketone VIII shows an IR band at 1705 cm⁻¹ and UV maxima at 220 and 269 mµ, characteristic of a bicyclo[3.1.0]hex-3-en-2-one system, \ddagger and its NMR spectrum shows five singlets at τ 3·10 (1H, O=C-C=C-H), 5·51 (1H, H-C-OAc), 8·08 (3H, OAc), 8·78 (18H, 2C(Me_3), and 8·88 (9H, C(Me_3)). The structure VIII for the ketone was based on the spectral data. The dienone IX was also obtained by the photolysis of VIII. However, IX was considerably stable to light, and long irradiation of IX did not form the acetoxyphenol X but gave an unknown product. These facts indicate that the bicyclo-ketone VIII is an intermediate leading onward to the dienone IX in the photolysis of VIa, and that the acetoxyphenol X is not formed photochemically from IX but by thermal or silica gel-catalyzed decomposition during isolation.

Photolysis of VIb. Irradiation of VIb in petroleum ether under similar conditions to those mentioned, followed by column chromatography on silica gel, yielded an isomeric dienone XI (16%) analogous to IX, an isomeric phenol XII (14%), an acetoxyphenol XIII (13%) and ketone XIV (9%), together with the unreacted starting material VIb (12%). Rapid chromatographic separation of the irradiation products on silica gel column gave the dienone XI in a higher yield (41%), while chromatography of the reaction mixture on florisil afforded the isomeric phenol XII in 39% yield. The dienone XI is unstable even under neutral conditions and is slowly converted to the isomeric phenol XII on standing at room temperature. The phenol XII was also formed quantitatively by the catalytic action of neutral alumina or florisil to the dienone XI. However, pyrolysis (250–260°) or acid-catalyzed decomposition of the dienone XI resulted in loss of a t-butyl group to yield the phenol XIII. The phenol XIII was synthesized by partial acetylation of 4-methyl-5-t-butylresorcinol obtained

[†] For the para-ketone tautomer of phenols, see Ref. 8.

[‡] For more details on the spectral data of bicyclo[3.1.0]hex-3-en-2-one, see Refs cited in a review.⁹

by t-butylation of 4-methylresorcinol.[†] In this case, it is certain that acetylation of a less hindered OH group is more favourable.

The IR band of the dienone XI at 1663 cm^{-1} with a shoulder at 1685 cm^{-1} (neat film) and its UV absorption at 318 mµ with a shoulder at 376 mµ indicate that it has a 2,4-cyclohexadienone skeleton. The NMR spectrum of the dienone XI showed four singlets at τ 3.58 (1H, 7.88 (3H, OCOCH₃), 8.83 (9H, a t-butyl) and 9.03 (9H, a t-butyl), a doublet at τ 8.29 (3H, J = 1 c/s) and a quartet at τ 7.21 (1H, J = 1 c/s).‡ From these physical properties and the facile conversion of the dienone XI to the phenols XII and XIII, the structure of the dienone should be represented by formula XI which is the ortho-ketonic tautomer of the phenol XII.

The structure of the ketone XIV was derived from its spectral and chemical properties. The ketone XIV shows an IR band at 1700 cm⁻¹ and UV absorptions at 223 mu and 265 mu characteristic of a bicyclo[3.1.0]hex-3-one-2-one system and NMR signals at τ 3·24 (1H, d, J = 1.5 c/s), 7·86 (1H, broad s), 7·99 (3H, s, Ac), 8·61 (3H, s, Me), 8.83 (9H, s, a t-Bu) and 8.94 (9H, s, a t-Bu). Treatment of XIV with sodium borohydride in methanol at 50° afforded a cyclopentenone XV and acid-catalyzed reaction of XIV yielded a cyclopentenone XVI isomeric with XV. The ketones XV and XVI were cyclopentenones according to their IR bands at 1704 and 1715 cm⁻¹, respectively, and by their UV spectra (Table 1) which indicate that they are α_{β} unsaturated ketones. The NMR spectrum of the cyclopentenone XV exhibits a AB quartet at τ 7.44 (2H, J = 19 c/s, a methylene), and three singlets at τ 2.71 (1H, H-C-C-C-O), 8.58 (3H, Me) and 8.80 (18H, two t-Bu groups). The ketone XVI shows NMR signals at τ 2.85 (1H, d, J = 2.6 c/s), 6.41 (1H, d, J = 2.4 c/s), 7.10 (1H, m) and 8.80 (3H, d, J = 4 c/s) which indicate that XVI possesses a partial structure O-C-C-CH-CH(CH₃)-CH-. The physical data of the ketones derived from the ketone XIV were consistent with the assigned structures, XV and XVI.

Mechanistic consideration. As discussed above, it is clear that the photoaromatization of VIa leading onward to the phenol X proceeds via the bicyclo[3.1.0]hex-3-en-2one VIII which further photochemically rearranges to the dienone IX, the precursor of the phenol X (Scheme 1).



† t-Butylation of resorcinol under the same conditions as those in the case of 4-methylresorcinol gave 4,6-di-t-butylresorcinol. Although 4-methyl-6-t-butylresorcinol was not isolated in a pure form because of its great sensitivity to air, its structure was confirmed by the NMR spectrum which showed five singlets at τ 2.93 (1H), 3.77 (1H), 4.75 (2H, broad signal), 7.87 (3H), and 8.64 (9H) together with several very small peaks due to some impurities.

[‡] For the long-range coupling between H_A and H_B of compounds having a partial structure i, see Ref. 9. It should be also noted that the protons of methyl group of VIb do not couple with the 3-proton, but with the 5-proton.

$$H_A - C - C = C - C - H_B$$

The photochemical formation of the bicyclo[3.1.0]hexenone XIV from VIb can be rationalized by a skeletal rearrangement involving 1,6-bond fission. Analogous transformation of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (IV) into the bicyclo-[3.1.0]hexanone V (Eq. 3) has been recently reported.⁴ From the fact that the dienone XI and the phenol XII could not be detected in the photolytic mixture of the ketone XIV, XIV is not considered to be an intermediate in the formation of dienone XI. On the other hand, although a bicyclohexenone XVII, analogous to VIII, could not be isolated in the case of the photolysis of VIb, it may be suggested that the photo-aromatization of VIb also proceeds via the bicyclohexenone XVII which is further transformed to XI, XII, and XIII (Scheme 2). An alternative possibility that the phenol XII is a precursor of the dienone XI is clearly eliminated, since XII was recovered unchanged on irradiation.



From the above consideration, it seems reasonable to assume that the mechanism for the photoaromatization of 2,4,6-trialkyl-6-acetoxy-2,4-cyclohexadienone (XVIII), including the 2,4,6-trimethyl analog (I)³, may be represented by a general mechanism as shown in Scheme 1. Although it is not clear at this moment whether the primary process in the transformation of XVIII involves n,π^* or π,π^* excitation, it may be rationalized that a bicyclo[3.1.0]hex-2-en-3-one XXI corresponding to VIII and XVII is formed by rearrangement of an intermediate XX analogous to the zwitterion IIb postulated originally by Barton and Quinkert³ for the photoaromatization of I. The bicyclohexenone XXI would further rearrange photochemically to form a ketone-tautomer XXIV via intermediates XXII and XXIII.¹¹ At the final stage of the reaction, XXIV aromatizes either with or without elimination of 6-alkyl group, depending upon steric situation.



There are a number of examples in which unstable compounds can be stabilized by introducing t-Bu groups.[†] Stability of the dienones IX and XI may be due to relieving from highly strained structures in their phenolic form. However, the dienone XI in which one of the t-Bu groups of IX is replaced by a Me group is less stable than the dienone IX and easily isomerizes to its phenolic form (XII). The dienone IX which is more strained in its phenolic form can aromatize to the acetoxyphenol X only accompanied by de-t-butylation.

 \dagger For example, Dewar-type benzenes,¹² cyclopentadienones,¹³ bicyclo[2.1.0]pentan-2-ones,¹⁴ and the para-ketone tautomer of phenols.⁸

EXPERIMENTAL

Oxidation of 2,4,6-tri-t-butylphenol with Pb(OAc)4

A mixture containing 32 g Pb(OAc)₄ (ca. 90%) and 13 g 2,4,6-tri-t-butylphenol in 100 ml benzene was stirred at room temp under N₂ for one day. Excess of the reagent was reduced by the addition of 5 g KI in 5 ml AcOH, and then 100 ml water was added. The ppt deposited was filtered off and washed with benzene. The filtrate was extracted with benzene. The organic layer was washed with Na₂S₂O₃aq, then with water and dried over Na₂SO₄. Evaporation of the solvent under reduced press gave yellow crystals. Recrystallization from MeOH afforded 5.94 g of VIa as yellow crystals, m.p. 96.5–98.5 , which, on further recrystallization from MeOH, gave yellow crystals, m.p. 98–99° (lit.¹⁶ m.p. 97–98°). (Found: C, 74.54; H, 10-22. Calc for C₂₀H₃₂O₃: C, 74.96; H, 10-06%).

The mother liquor was evaporated and the residue was chromatographed on 200 g neutral alumina (Act. I). Elution with 600 ml pet. ether gave 7.75 g yellow oil containing VIa and VIIa. Further elution with 100 ml pet. ether (b.p. 40–70°), then with 400 ml ether afforded 1.83 g of VIa as yellow crystals. The above-mentioned yellow oil was rechromatographed on 150 g neutral alumina Elution with 50 ml pet. ether yielded 4.06 g yellow crystals, which, by recrystallization from MeOH, gave VIIa as pale yellow crystals, m.p. 76–77.5° (lit.¹⁶ m.p. 52°). (Found: C, 75.24; H, 10-21. Calc. for $C_{20}H_{30}O_3$: C, 74.96; H, 10-06%).

Further elution with 200 ml pet. ether yielded 1.63 g of a mixture of VIa and VIIa. Elution with 200 ml pet. ether and 300 ml ether gave 1.235 g yellow crystals, which were identified as VIa (by IR). The total yields of VIa and VIIa amounted to 57% and 26%, respectively.

Hydrolysis of VIIa to 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadienone

A soln containing 50 mg of VIIa in 5 ml 0-5N KOH-EtOH was allowed to stand at room temp overnight. Addition of 5 ml water afforded 37 mg (85%) pale yellow needles, m.p. $113-125^{\circ}$ (lit.¹⁵ m.p. $133-134^{\circ}$), which were identified as 2,4,6-tri-t-butyl-4-hydroxy-2,5 cyclohexadienone (h IR and mixture m.p.).

Oxidation of 2,6-di-t-butyl-p-cresol with Pb(OAc),

A mixture containing 10 g 2,6-di-t-butyl-p-cresol, 24 g Pb(OAc)₄, and 100 ml AcOH was stirred at room temp under N₂ for 1 hr, giving a yellow soln. After standing for 2 days, the mixture was diluted with 100 ml water and extracted with CH₂Cl₂ (100 ml \times 3). The organic layer was washed with NaHCO₃ aq, then with water and dried over Na₂SO₄. Evaporation of the solvent under reduced press gave a yellow oil, which was chromatographed on 150 g silica gel. Elution with 120 ml benzene-pet. ether (1:1) yielded 118 mg yellow oil which was not further investigated. Further elution with 400 ml pet. ether-benzene (1:1) afforded 6:64 g crystals. Recrystallization from MeOH gave 3:81 g of VIIb as pale yellow crystals, m.p. 75-76° (lit.¹⁶ m.p. 76-77°). (Found: C, 73·24; H, 9·44. Calc. for C₁₇H₂₆O₃: C, 73·34; H, 9·41%).

Elution with 900 ml pet. ether-benzene (1:1), then with 800 ml benzene gave 4.63 g yellow oil which, on rechromatography on 80 g silica gel, afforded 3.01 g yellow oil. This oil was purified by short-path distillation $(75^{\circ}/10^{-3} \text{ mm Hg})$ and crystallized from MeOH to afford VIb as yellow crystals, m.p. $41-43.5^{\circ}$ (lit.¹⁶ an oil). (Found: C, 73.43; H, 9.11. Calc. for C₁₇H₂₆O₃: C, 73.34; H, 9.41%). The total yields of VIb and VIIb amounted to 24% and 53%, respectively.

Photolysis of 2,4,6-tri-t-butyl-6-acetoxy-2,4-cyclohexadienone (VIa)

A soln containing 1.50 g of VIa was irradiated under bubbling N_2 using a 450-W high-pressure mercury arc lamp (Ushio UM 450) with a water-cooled Pyrex jacket for 17 hr. After evaporation of the solvent, the residual oil was chromatographed on 40 g silica gel. Elution with 15 ml benzene gave 194 mg oil containing some crystals. Crystallization from MeOH afforded 60 mg (7%) colorless plates, m.p. 120–125°, which were identified as 2,4,6-tri-t-butylphenol (by IR and mixture m.p.). Further elution with 15 ml benzene yielded 125 mg brown oil which was not further investigated. Elution with 130 ml benzene gave 506 mg pale yellow solid. Recrystallization from MeOH yielded 225 mg of VIII as colorless plates, m.p. 75–76°. (Found : C, 74.68; H, 9.97. Calc. for C₂₀H₃₂O₃: C, 74.96; H, 10.06%).

The mother liquor, on rechromatography on silica gel, gave 116 mg of VIII. The total yield of VIII amounted to 23%.

Further elution with 100 ml benzene yielded 114 mg (8%) yellow crystals which were identified as the starting material (by IR). Elution with 100 ml benzene afforded 122 mg (8%) yellow crystals which, by recrystallization from MeOH, gave 60 mg of IX as yellow crystals, m.p. 118–119°. (Found: C, 74.66; H, 10-13. Calc. for $C_{20}H_{32}O_3$: C, 74.96; H, 10-06%); mass spectrum *m/e* 320 (parent peak).

Further elution with 100 ml benzene gave 98 mg yellow oil containing some crystals. Recrystallization

from pet. ether yielded 40 mg of X as colorless plates, m.p. 180–181^{\circ}. (Found: C, 73·11; H, 9·24. Calc. for C₁₆H₂₄O₃: C, 72·69; H, 9·15%). Removal of the solvent of the mother liquor gave yellow crystals which were shown by IR to consist of mainly IX. Elution with 300 ml benzene afforded 123 mg pale yellow crystals, which, on recrystallization from pet. ether, yielded 80 mg of X. The total yields of IX and X amounted to 12% and 13%, respectively.

Photolysis of VIa was also carried out in pet. ether under similar conditions. A chromatographic separation of the reaction mixture on silica gel gave 2,4,6-tri-t-butylphenol (2%), the isomeric ketone VIII (28%), the isomeric dienone IX (4%), and the acetoxyphenol (5%). Yields of the products, especially those of the isomeric dienone IX and the acetoxyphenol X, were not reproducible. This fact may be due to the instability of the isomeric dienone IX at relatively high temp and under an acidic condition.

Acetate of X. The acetate was prepared by the usual manner using Ac₂O and pyridine. Recrystallization of the product from MeOH gave as colorless crystals, m.p. 139.5–141°. The NMR spectrum (CDCl₃): τ 2.69 (1H, s), 3.29 (1H, s), 7.73 (6H, s) and 8.67 (18H, s). (Found: C, 70.68; H, 8.68. Calc. for C₁₈H₂₆O₄: C, 70.56; H, 8.55%). This compound was identified as the diacetate of 4,6-di-t-butylresorcinol (by IR and mixture m.p.), which was prepared by acetylation of 4,6-di-t-butylresorcinol.⁵

Photolysis of the ketone VIII

A soln of 50 mg of VIII in 70 ml benzene was irradiated under N_2 using a 100-W high-pressure mercury arc lamp (Ushio UM 102) with a water-cooled Pyrex jacket for 18 hr. Removal of the solvent gave a yellow oil which was separated by a preparative TLC on silica gel (Silica gel GF₂₅₄, Merck) into 11 mg of the ketone VIII and 19 mg of the dienone IX. (by IR).

Treatment of the dienone IX with acetic acid. A soln containing 10 mg of IX in 10 ml AcOH was allowed to stand at room temp for 5 hr. Addition of 2 ml water deposited 5 mg of a colorless solid, m.p. $165-175^{\circ}$, which was identified as X (by IR and mixture m.p.).

Photolysis of the dienone IX

A soln containing 10 mg of IX in 40 ml n-hexane (spectro-grade) was irradiated under bubbling N_2 using a 100-W high-pressure mercury arc lamp with a water-cooled Pyrex jacket and under cooling externally with ice-water. The progress of the reaction was followed by UV analysis. A new maximum near 250 mµ increased as a maximum at 315 mµ decreased, but a maximum at 276 mµ attributed to X could not be observed. After irradiation for 25 hr, the reaction product was found by a TLC on silica gel to consist of mainly two unknown compounds and the recovered diene IX, but not to contain the acetoxy-phenol X.

Photolysis of 2,6-di-t-butyl-4-methyl-6-acetoxy-2,4-cyclohexadienone (VIb)

(a) Separation of the reaction products by florisil chromatography. A soln of 826 mg of VIb in 300 ml pet. ether was irradiated under conditions described in the photolysis of VIa for 35 min. After removal of the solvent under reduced press, the reaction mixture was chromatographed on 70 g Florisil. Elution with 700 ml pet. ether-benzene (3:2) gave 138 mg yellow oil which was not further investigated. Further elution with 400 ml benzene yielded 319 mg (39%) yellow crystals, which on recrystallization from pet. ether, afforded 123 mg of XII as colorless crystals, m.p. 118-119°. Further recrystallization from pet. ether gave colorless crystals, m.p. 118-5–119°. (Found: C, 73·35; H, 9·11. Calc. for $C_{17}H_{26}O_3$: C, 73·34; H, 9·41%).

(b) Rapid separation of the reaction products. A soln containing 1.02 g of VIb in 300 ml pet. ether was irradiated under the conditions mentioned for 65 min. Two-thirds of the soln was evaporated under reduced press and then chromatographed on 40 g silica gel. Elution with 30 ml benzene gave 111 mg yellow oil which was not further investigated. Further elution with 50 ml benzene yielded 61 mg yellow crystals. Recrystallization from MeOH afforded 5 mg colorless crystals which were identified as XII (by IR). Elution with 100 ml benzene gave 52 ml yellow oil which was not further investigated. Further elution with 250 ml benzene and then with 100 ml CHCl₃ yielded 277 mg yellow oil. These fractions were eluted within 1.5 hr in order to minimize the facile rearrangement of the dienone XI to the phenol XII. This yellow oil was purified by a preparative TLC on silica gel and by a short-path distillation ($120^{\circ}/2$ mm) to give 106 mg of XI as a yellow oil. (Found: C, 73.66; H, 9-09. Calc. for C_{1.7}H₂₀O₃: C, 73.34; H, 9-41%).

(c) Separation of the reaction products by silica gel chromatography. A soln containing 760 mg of Vlb in 150 ml pet. ether was irradiated under bubbling N_2 using a 100-W high-pressure mercury arc lamp with a water-cooled Pyrex jacket for 1 hr. After removal of the solvent under reduced press, the residue was chromatographed on 20 g silica gel. Elution with 15 ml benzene gave 31 mg yellow oil which was not

further investigated. Further elution with 50 ml benzene yielded 92 mg (12%) yellow crystals. Recrystallization from pet. ether afforded 24 mg colorless crystals, which were identified as XII by IR. Elution with 30 ml benzene gave 38 mg yellow oil which was not further investigated. Further elution with 100 ml benzene yielded 118 mg (15.5%) yellow oil which was shown by its IR spectrum to consist mainly of the starting material VIb. Further elution with 50 ml benzene afforded 74 mg yellow oil which was shown by its IR spectrum and by TLC on silica gel to consist of XI and unreacted VIb. Elution with 150 ml benzene gave 123 mg (16.2%) yellow oil which was indicated by its IR spectrum to be XI containing a trace of the starting material VIb. Further elution with 100 ml benzene and then with 50 ml CH₂Cl₂ yielded 99 mg yellow crystals. Two recrystallizations from pet. ether afforded XIII as colorless crystals, m.p. $106.5-107.5^{\circ}$. (Found: C, 70.34; H, 8.46. Calc. for C₁₃H₁₈O₃: C, 70.24; H, 8.16%).

Further elution with 150 ml CH₂Cl₂ gave 60 mg (9·1%) pale yellow crystals. Recrystallization from pet. ether afforded XIV, as colorless crystals, m.p. 93·5–94°. (Found : C, 73·31; H, 9·41. Calc. for $C_{17}H_{26}O_{3}$ -C, 73·34; H, 9·41%).

Synthesis of the phenol XIII

(a) t-Butylation of 4-methylresorcinol. A mixture containing 1.0 g 4-methylresorcinol, which was prepared by reduction of β -resorcylaldehyde with amalgamated Zn and HCl,¹⁷ 1.85 g t-BuOH and 7 ml phosphoric acid was stirred at 50-60° for 7.5 hr, and after addition of 50 ml water, the reaction mixture was extracted with ether (100 ml × 3). The ethereal layer was washed with water, then dried over Na₂SO₄. Removal of the solvent gave a pale brown oil which was distilled at 160°/4 mm. This oil shows NMR signals at τ 2.93 (1H, s), 3.77 (1H, s), 4.75 (2H, broad s), 7.87 (3H, s) and 8.64 (9H, s) together with very small peaks of impurities.

(b) Partial acetylation of 4-methyl-6-t-butylresorcinol. A soln containing 140 mg 4-methyl-6-t-butylresorcinol, 100 mg Ac₂O and 0.5 ml pyridine was allowed to stand at room temp overnight and then was poured into 25 ml ice-water. After standing at room temp for several hrs, the mixture was extracted with ether (50 ml \times 3). The ethereal layer was washed with 1N HCl, then with water and dried over Na₂SO₄. Evaporation of the solvent gave 154 mg pale yellow crystals. Recrystallization from pet. ether gave colorless crystals, m.p. 103–105°, which was identical with XIII (by IR and mixture m.p.).

(c) Complete acetylation of 4-methyl-6-t-butylresorcinol. A soln containing 140 mg 4-methyl-6-t-butylresorcinol, 1 ml AcOH and 1 ml pyridine was allowed to stand at room temp overnight. Addition of 25 ml ice-water deposited 158 ml of a colorless solid. Two recrystallizations from pet. ether gave colorless crystals, m.p. 83.5–84°. (Found: C, 68.35; H, 7.52. Calc. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%). This compound was identified as the acetate of XIII which was prepared as above. (by IR and mixture m.p.).

Conversion of dienone XI into the phenol XIII

(a) By pyrolysis. The dienone XI (110 mg) was heated at 250-260° for 10 min. Short-path distillation (260°/18 mg Hg) of the product gave 89 mg reddish brown oil which, by crystallization from pet. ether gave 17 mg colorless crystals, m.p. 104-105°. These crystals were identified as XIII (by IR and mixture m.p.).

(b) By acid treatment. A mixture of 105 mg of XI and 2 ml 10% HBr in AcOH was allowed to stand at room temp for 2 min. After addition of 20 ml water, the mixture was extracted with ether ($25 \text{ ml} \times 3$) and the ethereal layer was washed with NaHCO₃ aq, then with water, and dried over Na₂SO₄. Removal of the solvent gave 78 mg reddish brown oil. Crystallization from pet. ether yielded 22 mg colorless crystals, m.p. 105–106°, which were identified as XIII (by IR and mixture m.p.).

(c) By silica gel treatment. The dienone XI (60 mg) was adsorbed on 5 g silica gel. After standing for 2 days, elution with 20 ml acetone gave a yellow oil, which was shown by its IR spectrum to consist mainly of XIII. Crystallization of the product from pet. ether afforded 7 mg colorless crystals which were identified as XIII (by IR).

Photolysis of the phenol XII

A soln containing 50 mg of XII in 40 ml pet. ether was irradiated under bubbling N_2 using a 100-W high-pressure mercury arc lamp for 1.5 hr. The reaction mixture was shown by TLC on silica gel and by its IR spectrum to consist mainly of XII, but no dienone IX was detected.

Photolysis of the ketone XIV

A soln containing 55 mg of XIV was irradiated under the conditions described for 1.5 hr. The reaction

mixture did not exhibit a UV absorption near 315 m μ and an IR band near 1650 cm⁻¹. and was shown by a TLC analysis to contain neither the dienone XI nor the phenol XIII.

Treatment of the ketone XIV with NaBH₄

A soln containing 135 mg of XIV and 100 mg of NaBH₄ in 10 ml MeOH was warmed at ca. 50° for 3 hr. After addition of 20 ml water, the mixture was extracted with ether (25 ml \times 3). The ethereal layer was washed with water and dried over Na₂SO₄. Evaporation of the solvent gave 95 mg yellow oil. This oil was separated by a preparative TLC on silica gel and gave 45 mg pale yellow crystals, which were purified by sublimation (50°/2 mm Hg) to give XV as colorless crystals, m.p. 50·5–52°. (Found : C, 76·51; H, 10·39. Calc. for C₁₅H₂₄O₂; C, 76·22; H, 10·24%). The starting material XIV (21 mg) was also obtained. The ketone XIV was recovered unchanged by warming in MeOH without NaBH₄.

Acid treatment of the ketone XIV

A soln of 210 mg of XIV containing a minute amount of XIII in 10 ml 10% HBr-AcOH was allowed to stand at room temp overnight. After addition of 30 ml water, the mixture was extracted with ether (50 ml \times 3). The ethereal layer was washed with NaHCO₃aq, then with water and dried over Na₂SO₄. Removal of the solvent gave a brown oil which was chromatographed on 12 g silica gel. Elution with 40 ml benzene yielded 9 mg yellow oil which was not further investigated. Further elution with 75 ml benzene afforded 67 mg pale yellow crystals which were purified by a short-path distillation (70–80°/2 mm) to give XVI as colorless crystals, m.p. 71–73°. (Found : C, 76-25; H, 10-40. Calc. for C₁₅H₂₄O₂: C, 76-22; H, 10-24%).

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