A limitation in the above kinetic analysis is that the quasi-two-dimensional nature of the reaction in multilayer samples has not been taken into account. There are two ways in which this circumstance may manifest itself.

(1) The spin label, which has a diffusion coefficient $\sim 10^{-7}$–10^{-8} cm^2/s in the fluid phase,[4] is essentially "immobile" with respect to the alkyl radicals. Thus a "diffusion-controlled" rate constant may be lowered by a factor of 2 compared to the case where both molecules are equally mobile.

(2) The spin label is constrained to move strictly in the plane of the membrane head-group region, and the free water-soluble molecules are constrained to move in a strip which is only ~20 Å wide, hence nearly but not strictly two-dimensional. The collision probability per unit time, and hence the rate constant, is then enhanced over the three-dimensional case.[15-18] It is difficult to predict the magnitude of this effect precisely but it is not likely to be more than a factor of the order of 4.[18]

Considering the magnitudes of these effects, and the fact that they work in opposite directions, we conclude that the order of magnitude variations we have observed cannot be due to such effects. In more detailed studies they should be considered quantitatively. Non-membrane-bound, water-soluble spin labels can be readily included in multilayer preparations, so that the kinetics with such species can be compared to the membrane-bound case. It is interesting to note that this affords a system for the study of two-dimensional reaction kinetics.[15-18]

There are other useful properties of this reaction which are not dealt with here experimentally, but which the kinetic analysis makes explicit. The fact that the homolysis is reversible in a step of rate comparable to the "forward" irreversible step (k_2) is of the utmost importance, since it allows one to control the lifetime of the alkyl radicals by varying the concentration of $Co(CN)_5^{3-}$.[19] This feature makes the reaction suitable for time-resolved studies of fast processes by flash photolysis.

References and Notes

(1) This work has been supported by the National Science Foundation (Grant PCM 77-23586).

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Products and Transients in the Photolysis of Methylated 2-Indanones. Observation and Kinetics of *o*-Xylylenes

K. Kamal de Fonseka, John J. McCullough,* and A. John Yarwood

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

Received July 3, 1978

Abstract: Transients assigned as *o*-xylylenes have been observed in the flash photolysis of a series of methylated 2-indanones. Thus, 1,1,3,3-tetramethyl-2-indanone gives a transient, assigned as 7,7,8,8-tetramethyl-*o*-xylylene (absorption maximum at 350 nm), while 1,1-dimethyl-2-indanone gives a transient with absorption maximum at 360 nm, assigned as 7,7-dimethyl-*o*-xylylene. Both these transients decay (thermally and photochemically) by a 1,5-hydrogen shift to yield alkyl isopropenylbenzenes. The rates of thermal decay are 0.0020 and 0.038 s^{-1} for the tetra- and dimethyl compounds, respectively, at ca. 20 °C in deoxygenated hexane. The decay of tetramethyl-*o*-xylylene showed a kinetic isotope effect (k_H/k_D) of 5.4. Activation parameters were $E_a = 19$ kcal/mol, $\Delta S^{\circ\ddagger} = -7.7$ eu (tetramethyl-*o*-xylylene); $E_a = 15.5$ kcal/mol, $\Delta S^{\circ\ddagger} = -13.9$ eu (dimethyl-*o*-xylylene). Photolysis of 1,1,3,3-tetramethyl-4,5-benzindan-2-one gives the thermally stable 9,9,10,10-tetramethyl-1,2-naphthoquinodimethane, which decays photochemically to 1-isopropenyl-2-isopropylnaphthalene. A transient with a lifetime of about 5 μs could be observed in the flash photolysis of 1,1,3,3-tetramethyl-5,6-benzindan-2-one, which gives two photoproducts: 2-isopropyl-3-isopropenylnaphthalene and 3,3,4,4-tetramethylnaphtho[*b*]cyclobutene. The rates of thermal decay of the transients are consistent with thermochemical calculations. Spectroscopic evidence, together with theoretical calculations, indicates that the transients are twisted about the "essential" single bonds of the nonaromatic ring, and cannot adopt the planar geometry necessary for the allowed suprafacial 1,5-H shift. This, together with the photolability of the transients, suggests that the thermal decay may involve the previously unknown antarafacial 1,5-hydrogen shift.

We have previously shown that the *o*-quinonoid species isoindenes can be generated by aryl migration on photolysis of 1,1-diarylindenes.[1] In the former study, we used kinetic isotope effects, substituent effects, and activation parameters to characterize the decay pathway of the isoindene transients. It was concluded that the data were consistent with a suprafacial 1,5-hydrogen shift (giving stable indenes) as the mode of decay. *o*-Quinonoid species have been produced by photolysis of various 2-indanones.[2] In a paper in 1966, Starr and Eastman[3] studied the photodecarbonylation of 1,1,3,3-tetra-

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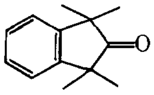
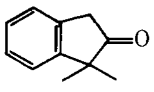
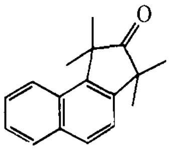
methyl-2-indanone (**1a**). The product obtained was 1-isopropenyl-2-isopropylbenzene, and it was suggested that a "biradical" intermediate gave this product by a hydrogen shift. In order to characterize both the transients in this reaction and the nature of the hydrogen shift by which they form stable product, we have studied the photochemistry of a series of methylated 2-indanones, **1a–d**. The products of irradiation of



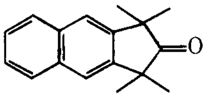
1a



1b



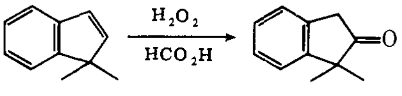
1c



1d

these indanones were characterized, and flash photolysis and kinetic spectroscopy were used to study the transient intermediates.

Synthetic Aspects. Preparation of the 2-Indanones. 1,1,3,3-Tetramethyl-2-indanone (**1a**) was prepared as described by Starr and Eastman.[3] 1,1-Dimethyl-2-indanone (**1b**) was obtained by the oxidation of 1,1-dimethylindene[4] with aqueous performic acid.

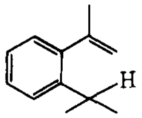


1b

The synthesis of 1,1,3,3-tetramethyl-4,5-benzindan-2-one (**1c**) followed Scheme I.

In this synthesis, the yield of **3** in the oxidation step was, unfortunately, very low. Therefore, two different approaches, not involving oxidation of an indene derivative, were adopted to obtain 5,6-benzindan-2-one (**1d**). One appraoch is shown in Scheme II. The barium salt pyrolysis was a low-yield reaction (3%). The benzindanone **6** decomposed on melting at 130 °C and was contaminated with 2,3-dimethylnaphthalene. This necessitated purification by chromatography. The tetramethyl ketone **1d**, in contrast, was quite stable thermally. These problems suggested the alternative synthetic approach, outlined in Scheme III, based on the ketone **7**.[8]

Steady-State Irradiation of the Indan-2-ones. Characterization of Products. Irradiation of 1,1,3,3-tetramethyl-2-indanone (**1a**) gives 1-isopropenyl-2-isopropylbenzene (**9**) as was originally reported by Starr and Eastman.[3] Similarly, 1,1-dimethyl-2-indanone (**1b**) gives 1-isopropenyl-2-methylbenzene (**10**) on irradiation.



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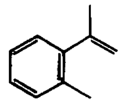
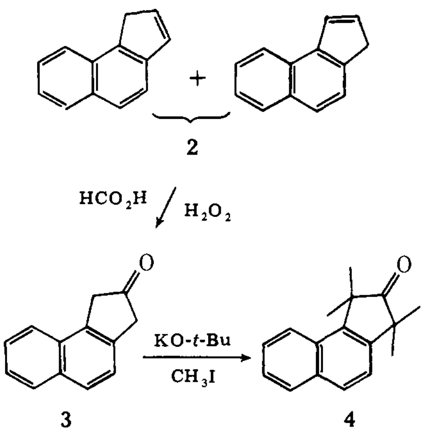


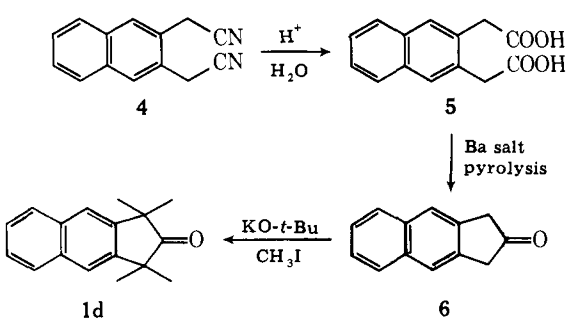
10

The latter (**10**) showed ^{1}H NMR resonances at δ 7.11 (m, 4 H, aromatics), 5.16 and 4.82 (multiplets, each 1 H, vinylic), 2.29 (s, 3 H, methyl), and 2.02 (d, $J = 2.0$ Hz, 3 H, methyl). The NMR and infrared spectra and the GC behavior were identical with those of an authentic sample, prepared by dehydration of 2-(2-methylphenyl)-2-propanol.[9]

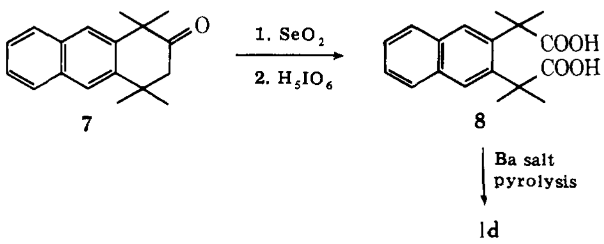
Scheme I



Scheme II

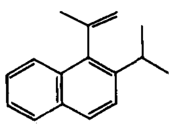


Scheme III

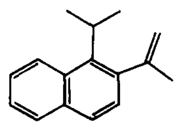


Irradiation of 1,1,3,3-tetramethyl-4,5-benzindan-2-one (**1c**) gives a single product, mp 110–112 °C, to which the structure 1-isopropenyl-2-isopropylnaphthalene (**11**) was assigned. The ^{1}H NMR showed resonances at δ 7.2–8.0 (m, 6 H, aromatics), 5.42 and 4.89 (each m, 1 H, vinylic), 3.30 (septet, $J = 7.0$ Hz, 1 H, methine), 2.08 (triplet, $J = 1$ Hz, 3 H, allylic methyl), 1.27 (d, $J = 7.0$ Hz, 3 H, isopropylmethyl), and 1.12 (d, $J = 7.0$ Hz, 3 H, isopropylmethyl). Irradiation of the septet at δ 3.30 caused the doublets at δ 1.12 and 1.27 to collapse to a pair of singlets.

Table I shows chemical shifts of isopropyl groups in various model compounds, data which were used in distinguishing between structure **11** and the alternative structure **12**. Notably, product **11** and 2-isopropenyl-3-isopropylnaphthalene (**13**, see below) have the isopropyl methine resonances at very similar fields (δ 3.30 and 3.22, respectively). The corresponding resonances in the isopropylnaphthalenes are 0.6 ppm apart with the methine resonance of 1-isopropylnaphthalene being at the lower field. Thus, we would expect the isopropyl methine resonance of **12** to be at lower field than in 1-isopropylnaphthalene, and assign structure **11** (rather than **12**) to the photoproduct.



11



12

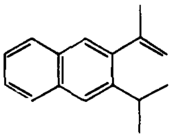
Table I. Comparison of Isopropyl Group Chemical Shifts (δ) with Those of Model Systems

compd	methine	methyl groups
1-isopropenyl-2-isopropylbenzene[a]	3.17	1.20
2-isopropenyl-3-isopropylnaphthalene[b]	3.22	1.27
1-isopropenyl-2-isopropylnaphthalene (**11**)	3.30	1.12, 1.27
1-isopropylnaphthalene[c]	3.62	1.31
2-isopropylnaphthalene[c]	2.97	1.30

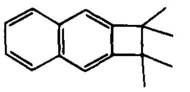
[a] Starr and Eastman (ref 3). [b] This work. [c] See ref 10.

It was observed that in the irradiation of **1c** secondary products began to appear after 60% conversion of starting material. These products were not investigated.

Irradiation of 1,1,3,3-tetramethyl-5,6-benzindan-2-one (**1d**) gave two products, in a ratio which varied with time. These products were separated by preparative GC, and were identified as 2-isopropenyl-3-isopropylnaphthalene (**13**) and 3,3,4,4-tetramethylnaphtho[*b*]cyclobutene (**14**).



13



14

The styrene derivative **13** had resonances at δ 7.2–7.8 (m, 6 H, aromatics), 5.17 and 4.89 (both m, both 1 H, vinylics), 3.21 (septet, $J = 6$ Hz, 1 H, isopropyl methine), 2.10 (d, $J = 1.0$ Hz, 3 H, allylic methyl), and 1.27 (d, $J = 6$ Hz, 6 H, isopropyl methyls).

The naphthocyclobutene **14** had mp 91–93 °C and showed NMR resonances at δ 7.2–7.8 (m, 6 H, aromatics) and 1.33 (singlet, 12 H, methyl groups).

The photolysis of **1d** is interesting in that it is the only reaction we have studied in which a benzocyclobutene product is obtained.[11] While product **14** is observed in the early stages of the photolysis of **1d**, it becomes the predominant product only after long irradiation times. In contrast, **13** is the major product early in the reaction, increases to a maximum as **1d** is depleted, and then disappears as **14** is formed. In a control experiment, done by GC using *trans*-stilbene as internal standard, it was shown that, while the ratio of **13**:**14** varied with time, their sum remained constant (see Experimental Section). The reactions shown in Scheme IV are invoked to explain the time dependence of the reaction mixture.

The ratio of **13**:**14** in the early stages of reaction is explained if $k_1 > k_2$. If, however, **13** absorbs light to return to the *o*-xylylene intermediate,[12] then conversion of **13** to the photochemically stable **14** would follow. Evidence for the intermediate *o*-xylylene and reasons for the formation of **14** in this reaction are discussed below.

Flash Photolysis. Identification and Kinetics of Intermediates. Flash photolysis of ketones **1a** and **1b** showed transients absorbing in the range 330–400 nm. In both cases the ketone absorption long-wavelength cutoff was about 330 nm, and the transient absorption (observed 30 μs after the photolysis flash) extended to 400 nm. In addition, irradiation of **1a** and **1b** at −78 °C using filtered light gave a sufficient buildup of transient for the λ_{max} to be recorded with the Cary 14 spectrophotometer. The spectrum from **1a** is shown in Figure 1.

The absorptions had λ_{max} at 350 (transient from **1a**) and 360 nm (transient from **1b**). We note that the absorption maximum of the parent *o*-xylylene **19** is at 375 nm.[11a] The transient from **1c** showed absorption beyond that of ketone (cutoff about 325 nm) extending to 350 nm. The λ_{max} of this transient was obscured by the ketone absorption and was not observed.

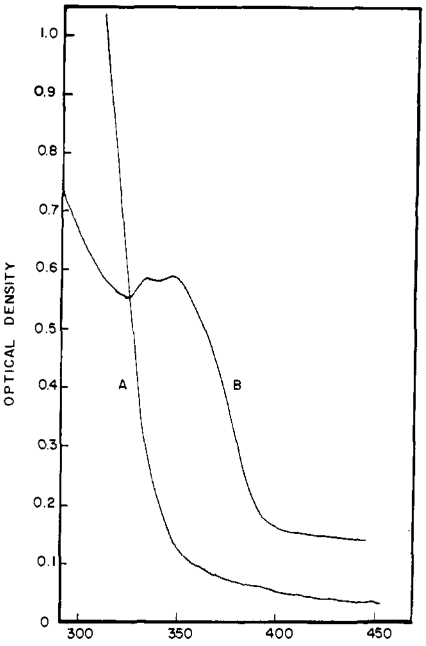
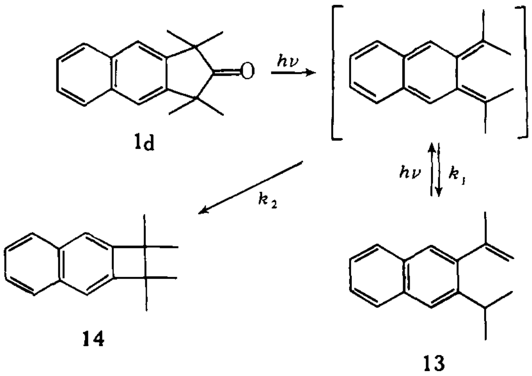


Figure 1. Spectra of 1,1,3,3-tetramethyl-2-indanone in hexane prior to (curve A) and after (curve B) photolysis at −78 °C. Ketone concentration in the photolysis was 0.068 × 10^{-3} *m*.

Scheme IV



The transient from **1d** was observed photographically, and the absorption appears in the range 500–550 nm. The λ_{max} should be about 525 nm, in reasonable agreement with that of 2,3-naphthoquinodimethane, which appears at 541 nm.[16] In the photolysis of **1d**, a second, shorter lived transient with absorption in the range 390–450 nm was also observed. We can only speculate as to the origin of this absorption, but it is possible that it is triplet–triplet absorption of the ketone **1d**. We have assigned these transients as the *o*-xylylenes **15–18**.

The spectra of **15** and **16** are in reasonable agreement with the assigned structures, if the probable nonplanar conformations of the latter are taken into account.[13] In the case of **17**, the absorption maximum is at short wavelength (>300 nm) and Hückel calculations show a large HOMO-LUMO gap for **17**, which is consistent with the short-wavelength absorption. The long-wavelength absorption of **18** is in reasonable agreement with a report of the spectrum of the parent 2,3-naphthoquinodimethane,[16] which has λ_{max} at 541 nm. Also the HOMO-LUMO gap in **18** is small (for details and results of calculations, see Experimental Section).

The decay kinetics of the transients were studied by kinetic spectrophotometry. The disappearance of the transient absorption was monitored as a function of time after the flash.

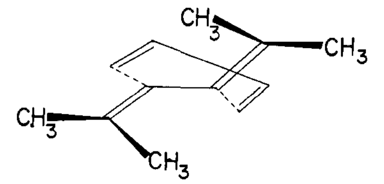
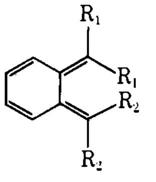
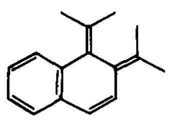


Figure 2. Nonplanar configuration of 7,7,8,8-tetramethyl-*o*-xylylene.

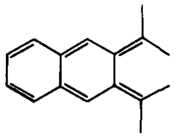
This study was possible only for the transients from **1a** and **1b**, i.e., **15** and **16**, for reasons which will be clear later.



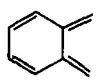
15, $R_1 = R_2 = CH_3$
16, $R_1 = H$; $R_2 = CH_3$



17



18



19

It was found that the decay of **15** and **16** was dependent on the light intensity of the monitoring beam, i.e., that the transients were subject to secondary photolysis. The following data were obtained for low (limiting) monitoring beam intensities. For **15**: decay rate constant (26 °C) = 3.9×10^{-3} s^{-1}; activation parameters E_a = 19.0 kcal mol^{-1}, $\Delta S^{\ddagger} = -7.5$ cal mol^{-1} K^{-1} (temperature range 20–50 °C). For **16** was obtained decay rate constant (26 °C) = 7.5×10^{2} s^{-1}; activation parameters, E_a = 15.5 kcal mol^{-1}, $\Delta S^{\ddagger} = -13.9$ cal mol^{-1} K^{-1}. Additionally, in the case of **15** a kinetic isotope effect was observed when $R_1 = R_2 = CD_3$. The ratio k_H/k_D (38.5 °C) was 5.4. The decay rates of **15** and **16** were unaffected by acid or base treatment of the cells or solutions.

Species **17** was long lived, surviving indefinitely in the dark at ambient temperature (~20 °C). Comparison of the absorption of a solution of **1c** before and after flashing showed the presence of absorption, additional to that of ketone **1c**, tailing to 350 nm. This absorption remained if the solution was kept in the dark, but was rapidly destroyed by light from the monitoring beam in the kinetic spectroscopy system.

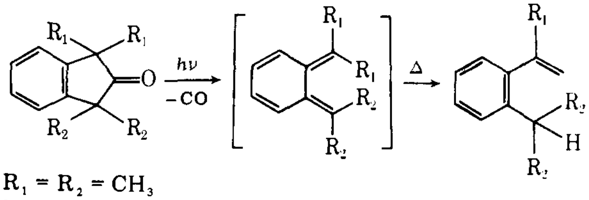
Species **18** was observed on flash photolysis of ketone **1d**. It was detected photographically, at the limit of detection of our system. We estimate that its lifetime is ~5 μs, from the delay between the photolysis and spectroscopic flashes required for observation. Thus, it is by far the shortest lived transient observed in these studies.

Attempts to trap the transients **15** and **16** were unsuccessful. Trapping agents included the dienophiles maleic anhydride, tetracyanoethylene, and α-chloroacrylonitrile. In all cases, intractable material was obtained when the ketone (**1a** or **1b**) was irradiated with the dienophile.

Discussion

All the accumulated information on the decarbonylation of 2-indanones is consistent with the mechanism in Scheme V. In the flash experiments, only one transient was detected, and this decayed with first-order kinetics in the case of **1a** and **1b**. The absorption spectra of the transients are consistent with the proposed *o*-xylylene structures, if nonplanar geometries are assumed for the latter[13] (see above results).

Scheme V



1a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$

The thermal decay of the *o*-xylylenes to styrene products is assumed to occur via a 1,5-sigmatropic hydrogen shift. In the case of a nonplanar *o*-xylylene as shown in Figure 2, the hydrogen shift must be antarafacial.

Such an antarafacial shift is ground state forbidden, and excited state allowed;[17,18] this would explain the relative slowness of the process compared to the isoindene–indene conversion,[1] and would account for the photolabile nature of these transients.

The kinetic isotope effect,[19] the negative entropies of activation,[1,20] and the activation energy[1,20] are all consistent with a concerted, sigmatropic hydrogen shift for the decay of these *o*-xylylenes.

The contrasting properties of **17** and **18** are of interest. Transient **17** is stable in the dark, while **18** has a lifetime of a few microseconds. Also, **18** apparently gives the product of cyclization **14** as well as styrene derivative **13** when it decays. Thus, **18** is the only transient we have studied which forms a benzocyclobutene such as **14**.

The properties of *o*-xylylene **18** seem to depend on two factors. The first is the large driving force toward aromatization of the two six-membered rings, which could account for the fast decay time of this species.[22] The second factor is the small HOMO–LUMO gap in **18**, compared with the other *o*-xylylenes. For example, the HOMO–LUMO gaps (Hückel calculations) are 0.59β, 0.72β, and 0.34β for *o*-xylylene, **17**, and **18**, respectively. These figures are for planar geometries. The small value of 0.34β would mean that the ground state of **18** should be close to the transition states for the symmetry-forbidden 1,5-hydrogen shift, and for the cyclization to benzocyclobutene **14**.[18]

In conclusion, we have observed transients, assigned as *o*-xylylenes in the photolysis of various methylated 2-indanones. These generally decay via a 1,5-hydrogen shift to give styrene derivatives. The decay process was characterized by activation parameters and a kinetic isotope effect. The hydrogen shift is very probably antarafacial and as such would be the first example of this process in the ground state.[18,24]

Experimental Section

Materials. All solvents were reagent grade and were distilled before use. Hexane was purified as described.[1] Tetrahydrofuran and benzene were distilled from lithium aluminum hydride; *tert*-butyl alcohol was distilled from calcium hydride. 1,1,3,3-Tetramethylindan-2-one was prepared by the procedure of Eastman and Starr.[3] The corresponding d_{12} compound was made similarly, using CD_3I (99.5% D, Stohler Isotope Chemicals).

Photochemical and Analytical Methods. All photolyses were done under argon in a Srinivasan-Griffin photochemical reactor (Rayonet), unless otherwise stated.

Column chromatography was on silica gel (60–200 mesh), "Baker Analyzed" reagent grade, or alumina (Fisher certified, neutral, 80–200 mesh).

Analytical gas–liquid chromatography (GC) was performed on a Varian-Aerograph Series 200 or a Tracor 560 dual column instrument with flame ionization detectors. The columns used on the Varian instrument were (a) 5 ft × ⅛ in. of 10% Carbowax 20M on 60–80 mesh Chromosorb W and (b) 5 ft × ⅛ in. of 5% QF-1 on Chromosorb W. The Tracor instrument was used with a 6 ft × ⅛ in. column of 8% QF-1 on 80/100 Chromosorb W. The flow rate of the carrier gas (helium) was ca. 31 mL min^{-1}. Integration of GC peak areas was performed using a Varian Aerograph Model 485 electronic digital integrator.

Preparative GC was on an Aerograph Model 200 dual column instrument with thermal conductivity detectors. A helium flow rate of ca. 60 mL min^{-1} was used with a 5 ft × 1/4 in. column of 7% QF-1 on Chromosorb W.

Proton nuclear magnetic resonance (NMR) spectra were obtained at 100 MHz on a Varian HA-100 spectrometer or at 90 MHz on a Varian EM-390 spectrometer. The solvent was chloroform-*d*, unless otherwise stated. The chemical shifts are δ values (ppm) measured downfield from tetramethylsilane which was the internal standard.

Infrared (IR) spectra were recorded with a Beckman IR-5 or a Perkin-Elmer 283 spectrophotometer. The solvent was spectrograde chloroform, unless stated otherwise. Ultraviolet spectra were on a Cary 14 spectrophotometer. Mass spectra were obtained using a CEC 21-100 mass spectrometer. Melting points were on a Kofler hot stage apparatus and are uncorrected.

Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.

1,1-Dimethylindan-2-one (1b). 1b was synthesized according to the method of Horan and Schiessler.[25]

1,1-Dimethylindene[4] (10 g, 69 mmol) was added dropwise to a solution of 30% hydrogen peroxide (10 mL, 96 mmol) in 50 mL of 90% formic acid at 50 °C. The resulting red solution was stirred at 55 °C for 6 h. The removal of solvent under reduced pressure yielded a viscous, red oil. This oil was added to a boiling solution of 7% sulfuric acid, steam was introduced, and the steam distillate was collected in an ice-cooled receiver. The distillate (300 mL) was extracted using methylene chloride (2 × 60 mL), and the extracts were dried (Na_2SO_4) and concentrated, giving 8 g of yellow oil which was purified by vacuum distillation (49 °C, 0.1 Torr). The yield of colorless liquid was 7 g (63%).

The UV absorption maxima (95% ethanol) occur at 274, 267, and 261 nm with decadic extinction coefficients of 1160, 1060, and 720, respectively. The IR spectrum includes peaks at 1750 (strained carbonyl), 1377, and 1354 cm^{-1} (*gem*-dimethyl). The NMR signals are at δ 7.15 (s, 4 H), 3.38 (s, 2 H), and 1.20 (s, 6 H).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.47; H, 7.50.

4,5-Benzindan-2-one (3). A mixture (ca. 50%) of 4,5- and 6,7-benzindenes[5] (1 g, 6 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of 30% hydrogen peroxide (1 mL, 9.6 mmol) in 15 mL of 90% formic acid at 40 °C. The solution was stirred at 25 °C for 8 h and concentrated under vacuum, giving a pale brown solid (0.8 g), which was added to 150 mL of boiling 7% sulfuric acid and steam distilled. The distillate (600 mL) was filtered, giving 70 mg (6%) of white crystals. Extraction of the filtrate with methylene chloride did not yield additional material. Recrystallization from ethanol gave colorless needles of **3** melting at 112-113 °C (lit.[6] 112-113 °C).

The IR spectrum shows the carbonyl absorption at 1751 cm^{-1}. The NMR signals are at δ 3.70 (s, 2 H), 3.80 (s, 2 H), and 7.3-8.0 (m, 6 H).

1,1,3,3-Tetramethyl-4,5-benzindan-2-one (1c). Potassium (300 mg, 7.7 mmol) and dry *tert*-butyl alcohol (5 mL, 54 mmol) in 10 mL of dry tetrahydrofuran was heated to reflux under a nitrogen atmosphere until all the potassium had dissolved. The solution was cooled in ice, and to it were added, in rapid succession, 170 mg (0.93 mmol) of **3** in 5 mL of tetrahydrofuran and 1 mL (16 mmol) of methyl iodide. The mixture was refluxed for 3 h, cooled, and added to 100 mL of water, which was then extracted with methylene chloride (3 × 50 mL). The combined organic extracts were washed with 5% HCl and water, dried (anhydrous Na_2SO_4), and concentrated, giving 270 mg of crude **1c** which was purified by recrystallization from aqueous ethanol, giving colorless crystals, yield 200 mg (90%). An analytical sample was prepared by sublimation, mp 124-124.5 °C. The IR absorptions are at 1746 (carbonyl), 1382, and 1362 cm^{-1} (*gem*-dimethyl). The NMR signals are at δ 8.2-7.3 (6 H, m), 1.65 (6 H, s), and 1.40 (6 H, s). The UV maxima (log ϵ), hexane: 272 nm (3.7), 279 (3.8), 291 (3.6), 308 (3.0), 314 (2.9), 322 (3.2).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.91; H, 7.68.

Naphthalene-2,3-diacetic Acid (5). Naphthalene-2,3-diacetonitrile[7] (5.2 g, 25 mmol) in 25 mL each of sulfuric acid, acetic acid, and water was refluxed for 45 min. The mixture was added carefully to 150 mL of cold water and the resulting solid was filtered and dried, giving 5.7 g of crude **8**. Recrystallization from aqueous ethanol gave 5.3 g of colorless needles (87%), mp 220-237 °C. Repeated recrystallization did not improve the melting range. The NMR absorptions of the methylene protons are at δ 3.93 (in acetone-d_6). The IR signal appeared at 1705 cm^{-1} with a shoulder at 1730 cm^{-1}.

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.05; H, 5.06.

5,6-Benzindan-2-one (6). Diacid **5** (0.5 g, 2 mmol) was mixed intimately with 0.8 g (2.5 mmol) of hydrated barium hydroxide and a drop of water. The resulting paste was dried and heated to 400 °C in a sublimation apparatus under 0.1 Torr. The sublimate (90 mg) was essentially a mixture of 2,3-dimethylnaphthalene and the desired ketone **6**. Its ketone content depended on the individual experiment, and varied from 25 to 75%. The sublimates from several runs (900 mg) were combined and chromatographed on 3.0 × 30 cm of silica gel. Elution with 25% benzene-hexane yielded 2,3-dimethylnaphthalene, while the indanone **6** was eluted with 25% ethyl acetate-hexane. **6** was further purified by sublimation, yielding 120 mg of colorless crystals, mp 130 °C dec (sealed capillary), estimated yield 3%. The IR showed a signal at 1755 cm^{-1}. NMR: δ 3.77 (s, 4 H), 7.4-8.0 (m, 6 H).

Anal. Calcd for $C_{16}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.53; H, 5.66.

1,1,3,3-Tetramethyl-5,6-benzindan-2-one (1d). 1d was synthesized by two different routes. (a) The procedure used was the same as that for **1c**. Thus, 90 mg (0.49 mmol) of indanone **6** was methylated using 0.5 mL (8 mmol) of methyl iodide and 200 mg (5 mmol) of potassium in 5 mL of *tert*-butyl alcohol/10 mL of tetrahydrofuran. Sublimation of the crude reaction product yielded 90 mg (77%) of pale yellow crystals. Recrystallization from acetone-methanol yielded colorless needles, mp 176-177 °C (sealed capillary). NMR: δ 1.43 (s, 6 H), 7.4-8.0 (m, 6 H). The IR showed 1745 (C=O), 1360 and 1380 (*gem*-dimethyl) cm^{-1}. UV maxima (log ϵ) in hexane: 319 nm (3.19), 304 (3.15), 294 (3.53), 283 (3.70), 272 (3.66), 262 (3.53).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.97; H, 7.59.

(b) Diacid **8**[8] (650 mg, 2.2 mmol) and 880 mg (2.8 mmol) of hydrated barium hydroxide were mixed intimately with a drop of water, dried, and pyrolyzed at 350 °C in a sublimation apparatus under 0.1 Torr. The crude sublimate (330 mg) was recrystallized from acetone-methanol, yielding 240 mg (45%) of colorless crystals, which were identical with those formed as described in (a) above.

Steady-State Photochemistry. Irradiation of 1,1-Dimethylindan-2-one (1b). 1b (282 mg) in 20 mL of purified hexane (0.09 M) contained in a quartz tube was purged with argon and irradiated using 16 RPR 3000 Å lamps. A slow stream of argon was maintained through the solution throughout the irradiation. Aliquots were withdrawn periodically and assayed by GC on a Carbowax column at 130 °C. The irradiation was stopped after 5 h when ca. 70% conversion to a single product was shown. The solution was concentrated and filtered through alumina (11 × 0.5 cm), giving 75 mg of colorless oil, identical with the dehydration product[9] from 2-(2-methylphenyl)-propan-2-ol by NMR, IR, and retention time on GLC. NMR: δ 7.11 (m, 3 H), 5.16 (m, 1 H), 4.82 (m, 1 H), 2.29 (s, 3 H), 2.02 (d, $J = 2$ Hz, 3 H). The IR included peaks at 1645, 900 (terminal CH_2=), 1490, and 765 (ortho-disubstituted benzene ring) cm^{-1}.

Irradiation of 1,1,3,3-Tetramethyl-4,5-benzindan-2-one (1c). A solution of 110 mg of **1c** in 70 mL of purified hexane (6.6×10^{-3} M) contained in a Pyrex tube, under argon, was irradiated using 16 RPR 3000 Å lamps for 8 h. Assay by GC on a QF-1 column at 150 °C showed ca. 80% conversion to a main product and ca. 5% of secondary product. The main product was isolated by preparative GC on QF-1 at 120 °C (retention time 6 min, at a flow rate of 60 mL/min), yielding 35 mg (36%) of pale yellow crystals. Recrystallization from 95% ethanol, followed by sublimation to a cold-finger condenser at −78 °C, gave an analytical sample, mp 110-112 °C. The NMR spectrum (CCl_4) showed δ 8.0-7.2 (m, 6 H), 5.42 (m, 1 H), 4.89 (m, 1 H), 3.30 (septet, $J = 7$ Hz, 1 H), 2.08 (triplet, $J = 1$ Hz, 3 H), 1.27 (d, $J = 7$ Hz, 3 H), and 1.12 (d, $J = 7$ Hz, 3 H). IR (CCl_4): 1645, 1250, 1290, 1420, 880 cm^{-1}. The product was identified as compound **11**.

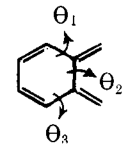
Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.40; H, 8.45.

Irradiation of 1,1,3,3-Tetramethyl-5,6-benzindan-2-one (1d). 1d (115 mg) in 25 mL of 7% benzene-hexane contained in a quartz tube was purged with argon and irradiated using 16 RPR 3000 Å lamps. Aliquots were withdrawn periodically and assayed by GC on a QF-1 column with temperature programming from 175 to 225 °C. The irradiation was stopped after 6 h when ca. 98% conversion to two

Table II

time, h	2.5	3.0	4.0	5.0	7.0	9.0
ratio **13**:**14**	2.26	1.74	1.42	1.09	0.50	0.17
ratio (**13** + **14**): stilbene	0.61	0.68	0.65	0.71	0.69	0.49

Table III. The Effect of Twisting about the "Essential" Single Bonds on the HOMO-LUMO Gap (ΔE) and the π-Electron Energy (E_π) of *o*-Xylylenes



structure	θ_1, deg	θ_2, deg	θ_3, deg	$\Delta E(\beta)$	$E_\pi(\beta)$
o-xylylene	0	0	0	0.589 92	9.953 96
	15	30	15	0.619 12	9.790 72
	30	60	30	0.710 44	9.395 96
2,3-naphthoquinodimethane	0	0	0	0.338 74	15.531 52
	30	60	30	0.389 30	14.962 40
1,2-naphthoquinodimethane	0	0	0	0.721 32	15.802 06
	30	60	30	0.858 38	15.269 62

products was seen. The products were separated by preparative GC on a QF-1 column at 110 °C, with a flow rate of 35 mL/min. The retention times were 62 and 72 min for the two products, identified as 2-isopropenyl-3-isopropylnaphthalene (**13**) and 3,3,4,4-tetramethylnaphtho[*b*]cyclobutene (**14**), respectively.

The styrene **13** was purified by preparative GC on a QF-1 column at 150 °C, giving 30 mg (30%) of colorless oil. NMR (CCl_4): δ 7.2-7.8 (m, 6 H), 5.17 (m, 1 H), 4.89 (m, 1 H), 3.21 (septet, J = 6 Hz, 1 H), 2.10 (d, J = 1 Hz, 3 H), 1.27 (d, J = 6 Hz, 6 H). IR: 1635, 1421, 1285, 1245, 860, and 690 cm^{-1}. The UV spectrum in hexane showed essentially naphthalene-type absorption, tailing to 355 nm. The high-resolution mass spectrum showed the parent ion at 210.1395 (calcd for $C_{16}H_{18}$, 210.1408).

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.41; H, 8.59.

The cyclobutene **14** was recrystallized from aqueous ethanol giving 10 mg (10%) of rhombic crystals, mp 91-93 °C. NMR (CCl_4): δ 7.2-7.8 (m, 6 H) and 1.33 (s, 12 H). IR: 1500-1400, 1375, 1370, 1290, 1250, 860, 690 cm^{-1}. The mass spectrum (60 °C, 80 eV) showed prominent peaks at *m/e* 210 (parent), 195 and 169 (loss of methyl groups).

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.20; H, 8.76.

Time Dependence of Photolysis of 1,1,3,3-Tetramethyl-5,6-benzindan-2-one (1d). Ketone **1d** (16.4 mg) in 7% benzene-hexane (20 mL) in a quartz tube was purged with argon and irradiated with eight RPR 3000 Å lamps. Aliquots (0.5 mL) were withdrawn at different times and mixed with 0.5 mL of a stock solution of *trans*-stilbene in ethyl acetate (1 mg/mL). The solution was evaporated and the residue redissolved in ~0.05 mL of ethyl acetate. The mixture was analyzed by GC on QF-1 at 160 °C. The ratio of the products (**13**, **14**) to each other and to the internal standard was measured by electronic integration. The results are given in Table II.

The ketone had essentially all reacted by the first aliquot. The ratio **13**:**14** steadily decreases with time, while the total (**13** + **14**) remains constant up to 7 h.

Low-Temperature Absorption Spectrum. A solution of 1,1,3,3-tetramethylindan-2-one (9 mg) in cyclopentane (0.7 mL), contained in a quartz NMR tube, was purged with argon and cooled to −78 °C in a quartz Dewar, normally used for phosphorescence spectra, which contained dry ice-methanol. The Dewar was immersed in a 0.45 M solution of $NiSO_4$, in 3 N H_2SO_4, contained in a quartz beaker. The whole assembly was irradiated using eight RPR 2537 Å lamps for 2.5 h, and the sample was poured into a vacuum-jacketed absorption cell of 4.5-cm path length containing 70 mL of pentane at −78 °C. The absorption spectrum was measured.

Flash Photolysis. The experiments were conducted as described previously[1] except that the Biomation waveform recorder was replaced by a Hewlett-Packard Model 7047 A *X-Y* recorder which facilitated the measurement of slower rates. The decay curves were obtained on chart and processed manually. Computation of the first-order rate constants was on the HP-3000 computer.

The effect of acid and base on decay time was studied as before[1] using a stock solution of 5 mg of **1a** in 100 mL of hexane. The cell and solution were washed with 3 N H_2SO_4 or 3 N NaOH prior to being flasked. Good first-order decay plots were obtained. The rate constants (36.4 °C, deoxygenated solution) follow: control, 0.0131 s^{-1}; acid treated, 0.0126 s^{-1}; base treated, 0.0129 s^{-1}.

Hückel Calculations. These were simple Hückel calculations performed on the CDC 6400 computer using a program kindly provided by Dr. D. P. Santry. The effect of twisting about bonds a, b, and c was studied by taking the dihedral angles (θ_1, θ_2, and θ_3) of twist from a space-filling model, and using resonance integrals which were given by $\beta_{ij}(\theta) = \beta_{ij}(0) \cos \theta$. The π energies and HOMO-LUMO gaps were calculated as a function of θ_1, θ_2, and θ_3 for *o*-xylylene, 2,3-naphthoquinodimethane, and 1,2-naphthoquinodimethane. The results are given in Table III.

Acknowledgments. We thank Dr. D. P. Santry for the program used in the Hückel calculations. We also thank McMaster University for a Benefactor Studentship to K. de Fonseka. Support of the research by the National Research Council of Canada is acknowledged.

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