of the intermediate ester: mp 84 °C (isopropyl ether); IR (KBr) 3250, 1730, 1620 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_2O_3$: C, 70.15; H, 7.65; N, 8.13. Found: C, 69.97; H, 7.65; N, 8.20.

A solution of 4 g of this ester and 1.6 g of KOH in 100 mL of ethanol was refluxed for 6 h. The residue left after the evaporation of the solvent was dissolved in water and washed with CH_2Cl_2. The aqueous solution was acidified with dilute HCl to liberate the acid, which was subsequently isolated by extraction with benzene. Recrystallization from a mixture of 2-propanol and isopropyl ether afforded 3.0 g (80%) of **6**: mp 132 °C; IR (KBr) 3340, 2800–2300, 1700, 1590 cm^{-1}; ^1H NMR δ 11.4 (s, 1 H, OH), 8.35 (s, 1 H, NH), 7.60–6.90 (m, 5 H, aromatic), 0.9 (t, 3 H, CH_3). Anal. Calcd for $C_{18}H_{22}N_2O_3$: C, 68.77; H, 7.05; N, 8.91. Found: C, 68.41; H, 7.00; N, 8.71.

(±)-(*E*)-Norvincamone. A mixture of 1.5 g of **6** and 8 mL of $POCl_3$ in 15 mL of toluene was refluxed under N_2 for 6 h. The solid[13] left after the evaporation in vacuo of the solvent and excess chloride was suspended in 120 mL of 65% aqueous acetic acid, treated slowly with 7 g of zinc powder, and stirred for 6 h. The filtered solution was extracted with CH_2Cl_2. The organic layer was stirred with 10% NaOH solution, separated, washed with water, and evaporated to give 0.78 g of **8** (58%): mp 64 °C (isopropyl ether); IR (KBr) 1795, 1665 cm^{-1}; ^1H NMR δ 7.7–7.85 (m, 1 H, aromatic), 7.1–7.5 (m, 3 H, aromatic), 4.3 (m, 1 H, C_{21}), 1.15 (t, 3 H, CH_3); MS *m/e* (relative intensity) 280 (M^+, 100), 265 (4), 252 (11), 251 (16), 224 (12), 223 (26), 222 (14), 212 (43), 210 (19), 208 (16), 195 (4), 167 (26); UV λ_{max} (EtOH) 295 nm, 260, 238, 200; ^{13}C NMR (performed on the hydrochloride in D_2O with Me_4Si as standard) δ 175 (CO), 135.2, 134.3, 133.3, 116.4, 121.4, 115.5, 111.8, 60.2, 53.9, 52.5, 45.1, 30.6, 27.3, 19.9, 17.7, 10.1. Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.07; H, 7.16; N, 9.99.

Amide Acid 9. This acid was prepared in 80% yield by hydrolysis of the corresponding ester,[9] as described for the preparation of **6**. For **9**: IR (KBr) 3400, 3600–2300, 1715, 1600 cm^{-1}; ^1H NMR δ 10.3 (s, 1 H, OH), 8.1 (s, 1 H, NH), 7.6–6.85 (m, 5 H, aromatic), 0.8 (t, 3 H, CH_3).

Immonium Salt 10. A suspension of 0.7 g of the amide acid **9** in 10 mL of toluene and 6 mL of $POCl_3$ was refluxed for 8 h under N_2. The solid left after evaporation in vacuo of the solvent and excess $POCl_3$ was dissolved in CH_2Cl_2 and stirred with 20 mL of an aqueous 1 M $LiClO_4$ solution. The separated organic layer was dried and evaporated to give 0.7 g (80%) of **10**, mp 220 °C (lit.[5a] mp 215–220 °C).

Reduction of 10. The salt **10** was reduced as described for the preparation of **8**. The products obtained (86% yield) were separated by chromatography on neutral alumina (eluant CH_2Cl_2) and identified as (±)-vincamone (**11**; 20%), mp 200 °C (lit.[5a] mp 200–202 °C), and *trans*-(±)-vincamone (**12**; 80%), mp 135 °C (lit.[5a] mp 135–136.5 °C).

Acknowledgment. We are indebted to Dr. M. Avramoff, Weizmann Institute of Science, Rehovot, Israel, for his helpful discussions in the preparation of the manuscript.

Registry No. (±)-**4**, 70672-14-9; (±)-**5**, 70672-15-0; (±)-**6**, 72036-10-3; (±)-**6** ethyl ester, 70672-16-1; (±)-**8**, 70672-25-2; (±)-**8**·HCl, 70672-26-3; (±)-**9**, 72036-11-4; (±)-**10**, 72074-19-2; (±)-**11**, 2580-88-3; (±)-**12**, 60384-17-0; tryptamine, 61-54-1.

(13) The instability of the intermediate immonium salt prevents its purification. The reduction must be performed with the crude product.

Benzo- and Naphthoquinone Adducts of Hexamethyl-2,4-cyclohexadienone. Synthesis, Enolization, and Rearrangements

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The benzoquinone adduct **2** of hexamethyl-2,4-cyclohexadienone is readily converted to its dienolic form **4** by sodium methoxide and base. In contrast, the analogous 1,4-naphthoquinone adduct **3** cannot be similarly converted to its dienolic form **7**. However, **3** can be aromatized under nonequilibrating conditions (sodium hydride followed by methyl iodide) to give the dimethyl ether **8**. Reflux of **2** in HBr–HOAc gives rearrangement product **9** as a consequence of enolization and 1,2-aryl migration. Only one isomer is formed, whereas acid-catalyzed rearrangement of the dimethyl ether **5** gives products corresponding to both aryl and vinyl migration (**11** and **12**). In contrast, in the naphthalene series **3** does not rearrange in acid, and its dimethyl ether **8** gives only **23**, the product of aryl migration. Adduct **2** on irradiation gives the product of intramolecular cycloaddition **25** and the oxa-di-π-methane rearrangement product **26** in a ratio which depends on solvent. Adduct **3** on irradiation gives only the latter type of product (**27**). Adduct **3** is readily oxidized in base and air to the novel epoxy trione **30**.

2,4-Cyclohexadienones react as dienes toward a variety of dienophiles[1,2] to provide a useful entry to bicyclic systems. Their reaction with quinones as dienophiles, however, has not been studied. We describe here adducts formed by reaction of benzoquinone and 1,4-naphthoquinone with hexamethyl-2,4-cyclohexadienone, their different enolization behavior, a novel acid-catalyzed rearrangement which they undergo, their photoisomerization, and several other of their transformations.

Results and Discussion

Treatment of hexamethyl-2,4-cyclohexadienone (**1**)[3] with benzoquinone or 1,4-naphthoquinone in refluxing toluene gave a good yield of crystalline adducts **2** and **3**, respectively. In each case a single stereoisomer was isolated, and

(1) Waring, A. J. *Adv. Alicyclic Chem.* **1966**, *1*, 223–8.
(2) Hart, H.; Collins, P. M.; Waring, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1005. Oku, A.; Kakihana, T.; Hart, H. *Ibid.* **1967**, *89*, 4554. Hart, H.; Ramaswami, S. K.; Willer, R. *J. Org. Chem.* **1979**, *44*, 1.

(3) Hart, H.; Lange, R. M.; Collins, P. M. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 598.

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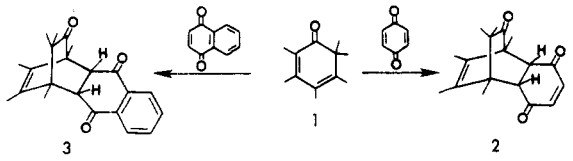
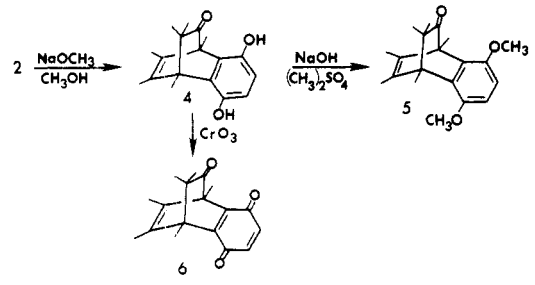
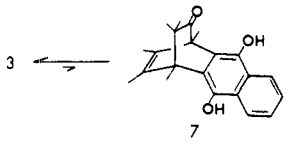


since photochemical transformations of **2** (vide infra) require the endo geometry, we assign this configuration to both adducts. Each adduct remained in the keto form, as shown by conjugated carbonyl bands in the infrared (1679 cm^{-1} for **2**, 1685 cm^{-1} for **3**) and by two doublets in the NMR spectra for the protons at the ring juncture.

Enolization of 2 and 3. Treatment of **2** with sodium methoxide in methanol, followed by acidification, gave the hydroquinone **4**, whose structure was clear from its spectra and from its conversion to the dimethyl ether **5** and quinone **6**.



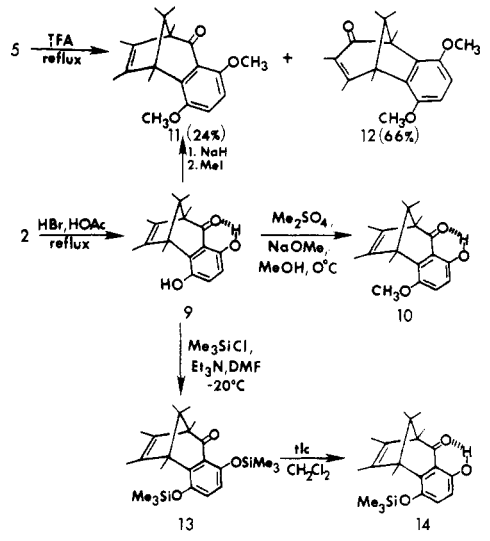
In contrast, similar treatment of **3** with base gave, after acidification, mainly a product containing one more oxygen and two less hydrogen atoms, obviously due to air oxidation (vide infra). When an inert atmosphere was maintained, only **3** was recovered on acidification, although the red color of the alkaline solution of **3** indicated that the dianion had probably been formed. Consequently, we conclude that in the protic solvent methanol the keto structure **3** is preferred over the corresponding aromatic hydroquinone structure **7**, whereas with the benzoquinone

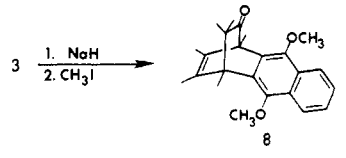


adduct the converse is true (**4** more stable than **2**). Less energy should be gained through aromatization of **3** than of **2** (second ring of naphthalene vs. a benzene ring), and apparently this energy in the case of **3** is less than twice the energy difference which ordinarily favors keto over enol structures. Since the enolic form is favored in 1,4-naphthalenediol and its 2,3-dialkyl derivatives,[4] however, another factor may also be important in the aromatization of **2** and **3**. When the enols **4** (and **7**) are produced, the CC bond which is part of the bicyclic ring system will be shortened. This bond shortening must introduce some additional strain and will cost energy. This factor is present in **7** but not in 1,4-naphthalenediol and may account for their different enolization behavior.

Compound **3** can be aromatized under nonequilibrating conditions. Treatment of **3** with sodium hydride in a mixture of benzene and DMF, followed by addition of methyl iodide, gave the dimethyl ether **8**. This ether could not be prepared from **3** using sodium methoxide and dimethyl sulfate in methanol.

Scheme I





Acid-Catalyzed Rearrangements. Brief reflux of **2** in acetic acid containing a little hydrobromic acid caused its isomerization to **9**. The structure of **9** is based on its spectra and on the structural correlations outlined in Scheme I.

The infrared spectrum of **9** showed bands for a free OH (3620 cm^{-1}) and for a hydrogen-bonded OH (3450 cm^{-1}) and a band at 1640 cm^{-1} consistent with a conjugated, hydrogen-bonded carbonyl group.[5] The ^1H NMR spectrum of **9** also showed peaks for a free (δ 4.13) and a hydrogen-bonded (δ 12.44) hydroxyl proton, as well as other peaks consistent with the assigned structure.

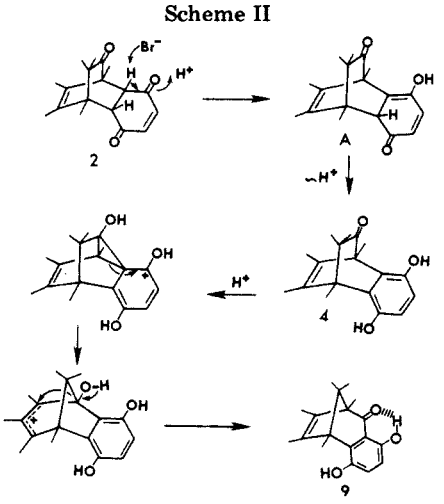
Treatment of **9** with sodium methoxide and dimethyl sulfate at 0 °C gave the monomethyl ether **10**, whose NMR spectrum still showed a hydrogen-bonded hydroxyl proton at δ 12.2. The hydroxyl proton peak at δ 4.13 in **9** was absent and replaced by a peak at δ 3.63 for the methoxyl protons. With sodium hydride followed by methyl iodide, **9** was converted to the dimethyl ether **11**, which had singlets for the two methoxyl groups at δ 3.64 and 3.73. The same dimethyl ether was obtained as the minor product of the acid-catalyzed rearrangement of **5**, the major product being the isomeric dimethyl ether **12**. It was possible to readily distinguish **11** from **12** by the chemical shifts of the allylic methyl groups. In **12**, these appear at δ 1.60 and 1.91, the latter being due to the methyl β to the carbonyl groups. In **11**, the allylic methyls appear at δ 1.40 and 1.53, relatively unaffected by proximity to or conjugation with the carbonyl group.

Both hydroxyl groups in **9** could be silylated to give **13**, which showed peaks at δ 0.17 and 0.27 for the two trimethylsilyl groups. However, attempts to purify **13**, even under very mild TLC conditions, resulted in hydrolysis of the trimethylsilyl group adjacent to the carbonyl, to give **14**. The NMR spectrum of **14** showed a hydrogen-bonded

(4) 1,4-Naphthalenediol (mp 192–5 °C) and its tautomer, 1,4-diketo-1,2,3,4-tetrahydronaphthalene (mp 98 °C), are discrete, isolable compounds (Thomson, R. H. *J. Chem. Soc.* **1950**, 1737. Bruce, D. B.; Thomson, R. H. *Ibid.* **1952**, 2759. Bloom, S. M.; Hutton, R. F. *Tetrahedron Lett.* **1963**, 1993), but treatment of the diketo form with base (i.e., triethylamine) converts it immediately and completely to the dienolic form. The thermal keto–enol equilibration of a number of 1,4-naphthalenediols was recently studied by: Pearson, M. S.; Jensky, B. J.; Greer, F. X.; Hagstrom, J. P.; Wells, N. M. *J. Org. Chem.* **1978**, *43*, 4617.

(5) Bellamy, L. J. "The Infra-red Spectra of Complex Molecules", 2nd ed.; Methuen and Co.: London, 1958; pp 96, 132.

Scheme II

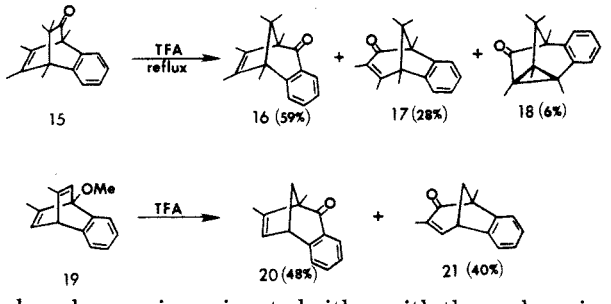


hydroxyl proton at δ 12.03 and one trimethylsilyl group at δ 0.47.

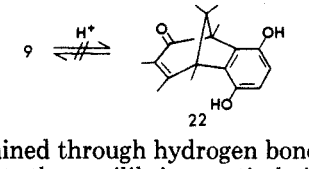
The conditions essential for the rearrangement of **2** to **9** are somewhat critical. The HBr cannot be omitted, nor can it be replaced by trifluoroacetic acid (TFA). However, if **2** is converted by base to the phenolic form **4**, then refluxing TFA will convert **4** to **9**. Thus it appears that the bromide ion supplied by HBr may be essential to the enolization of **2**, which we regard as the first step in its isomerization to **9**. A plausible mechanism is shown in Scheme II.

The independent isomerization of **4** to **9** shows that **4** is an allowed intermediate in the isomerization of **2** to **9**. However, we cannot exclude the possibility that A undergoes skeletal rearrangements (parallel to those shown for **4**) before the second enolization occurs.

Rearrangements similar to this one have been described previously.[6-9] The isomerizations of **15**[6] and **19**[9] are typical. In these cases, products are formed in which the

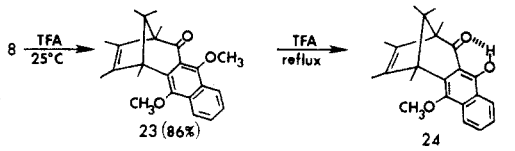


carbonyl group is conjugated either with the aryl or vinyl moiety (i.e., **16** and **17**, or **20** and **21**). Indeed, these products may equilibrate under the reaction conditions. In contrast, rearrangement of **2** or **4** gave *only* **9**; no **22**, which would be the product of vinyl rather than aryl migration, was observed, and separate treatment of **9** with acid (including H_2SO_4) did not give any **22**. Perhaps the



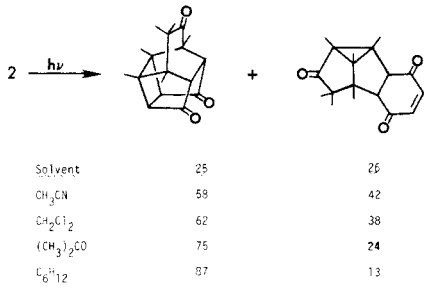
stabilization gained through hydrogen bonding in **9** is the factor which tilts the equilibrium entirely in its direction. Some evidence for this is our observation that the dimethyl ether **5** rearranged to a mixture of **11** and **12**, the latter predominating (Scheme I). The mechanism for the rearrangement of **5** is undoubtedly analogous to that of **15**.[6]

In the naphthalene series, the results were a little different. Treatment of **3** with HBr in acetic acid gave only recovered starting material. We attribute this result to the difficulty with which the enol of **3** (i.e., **7**, essential for the isomerization) is formed. Apparently this is true in acid as well as in base, as described above. However the dimethyl ether **8** does rearrange in acid. In TFA at room temperature, the product is exclusively **23** (aryl migration; contrast with **5**). At reflux, selective demethylation occurs to give the hydrogen-bonded product **24**. The preferred



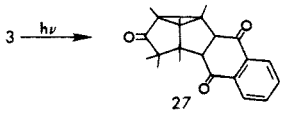
aryl migration in **8**, compared with preferred vinyl migration in **5**, may be due to the added charge delocalization which is possible in the intermediates because of the extra arene ring.

Photoisomerizations. Irradiation of **2** through Pyrex gave two products, **25** and **26**, in a ratio which was solvent dependent. The products arise from a $2\pi + 2\pi$ cyclo-



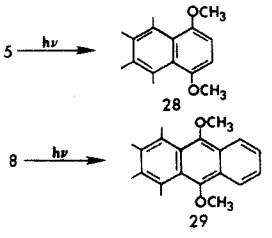
Solvent	25	26
CH_3CN	58	42
CH_2Cl_2	62	38
$(CH_3)_2CO$	75	24
C_6H_{12}	87	13

addition and an oxa-di-π-methane rearrangement, respectively, the former being favored by decreasing solvent polarity. In the case of **3**, the cycloaddition is not possible, and irradiation gave only the oxa-di-π-methane product **27**.



Both of these reaction types have ample precedent[10,11] and usually occur via triplet excited states. We have no explanation for the solvent effect on the **25**/**26** ratio.

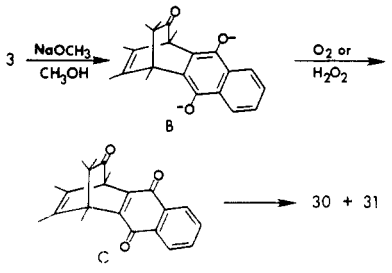
In contrast with **2** and **3**, irradiation of the methyl ethers of the dienolic form of these compounds (i.e., **5** and **8**) proceeded with loss of the carbonyl bridge (presumably as dimethylketene) to give aromatic products **28** and **29**.



This type of photoelimination also has precedent.[12] Al-

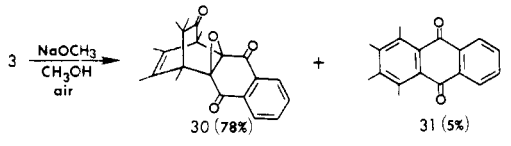
(6) Hart, H.; Love, G. M. *Tetrahedron Lett.* **1971**, 2267.
(7) Heaney, H.; Ley, S. V. *Chem. Commun.* **1971**, 224.
(8) Hales, N. J.; Heaney, H. *J. Chem. Soc., Chem. Commun.* **1975**, 83.
(9) Brown, D. S.; Heaney, H.; Ley, S. V.; Mason, K. G.; Singh, D. *Tetrahedron Lett.* **1978**, 3937.
(10) For reviews, see: Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. Dauben, W. G.; Lodder, G.; Ipaktchi, J. *Fortschr. Chem. Forsch.* **1975**, *54*, 73.
(11) Cookson, R. C.; Crundwell, E.; Hudec, J. *Chem. Ind. (London)* **1958**, 1003. Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3062.

Scheme III



though none of these photoreactions is novel, we point out that the quinone adducts of dienones can be useful in this manner for the synthesis of cage and polycyclic compounds and of naphthalenes, anthracenes, etc.

Miscellaneous Reactions. We alluded above to an oxidation product obtained in an attempt to produce **7** from **3** by treatment with base in the presence of air. We ascribe structure **30** to this product; the anthraquinone **31**



was also produced in small yield during this reaction. The formation of **30** and **31** occurred under very mild conditions and rapidly (0 °C to room temperature, 3 h). Treatment of **3** with base under nitrogen, followed by addition of 30% H_2O_2 at 0 °C, also gave **30**.

The structure of **30** is based on its elemental analysis and spectra. The mass spectrum of **30** had a parent peak 14 amu above that of **3**, corresponding to the addition of one oxygen atom and the loss of two hydrogens. It also showed intense fragmentation peaks corresponding to the loss of dimethylketene and this fragment plus an oxygen atom. The IR spectrum showed both nonconjugated (1725 cm^{-1}) and conjugated (1700 cm^{-1}) carbonyl groups, as well as bands at 1285 and 875 cm^{-1} attributable to an epoxide moiety. The NMR spectrum showed four aromatic protons and six methyl groups (two aliphatic at δ 0.92, 1.03; two allylic, homoallylically coupled, at δ 1.67 and 1.77; and two bridgehead, at δ 1.80). We cannot, from these data, distinguish **30** from its stereoisomer in which the epoxide ring is "down" instead of "up", but only one of the two compounds is formed.

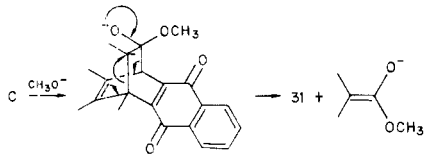
The formation of **30** and **31** can be rationalized as shown in Scheme III. The dianion B, formed from **3** and base, can be oxidized by either oxygen or hydrogen peroxide to the quinone C, which may suffer either of two fates.[13] Further oxidation[14] converts C to **30**. Alternatively, elimination of the ketone bridge will give **31**.[15]

(12) Murray, R. K., Jr.; Hart, H. *Tetrahedron Lett.* **1968**, 4995. Hart, H.; Murray, R. K., Jr. *Ibid.* **1969**, 379. Ipaktchi, J. *Ibid.* **1969**, 215.

(13) The air–base oxidation of quinone–diene adducts to quinones has precedent. See: Diels, O.; Alder, K.; Stein, G. *Chem. Ber.* **1929**, *62*, 2337.

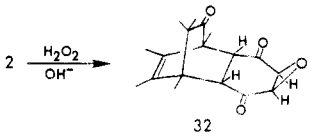
(14) If the oxidation is performed in air and base, oxygen will be converted to peroxide as a consequence of the transformation of B to C. Peroxide will thus be the epoxidizing agent for conversion of C to **30** whether the reaction is run in air or with hydrogen peroxide under nitrogen.

(15) This reaction probably occurs by attack of base on the nonconjugated carbonyl group:



The methyl isobutyrate was not isolated.

In contrast with **3**, treatment of **2** with alkaline hydrogen peroxide gave only the expected epoxide **32**.



Experimental Section

NMR spectra were recorded on a Varian T-60 or Bruker WH-180 spectrometer with $CDCl_3$, and chemical shifts are reported in parts per million (δ) from internal Me_4Si. Infrared spectra were measured on a Perkin-Elmer 237 grating spectrometer as CCl_4 solutions in 1-mm KBr cells. UV spectra were obtained with a Unicam SP-800 instrument. Mass spectra were obtained at 70 eV using a Hitachi Perkin-Elmer RMU-6 spectrometer. Melting points were uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

1,8,9,10,12,12-Hexamethyltricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-3,6,11-trione (2). A solution of 10 g (0.056 mol) of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one[3] and 6.1 g (0.056 mol) of *p*-benzoquinone in 25 mL of toluene was stirred at reflux under nitrogen for 36 h, after which the reaction mixture was concentrated under vacuum. The resulting solid residue was dissolved in 200 mL of ether and washed with water; the black decompositon solid found between the two layers was discarded. The ether layer was dried ($MgSO_4$) and rotary evaporated to give a yellow solid, which was recrystallized from 95% ethanol, mp 113.5–114 °C. A total of 13.4 g (83%) of **2** was obtained: IR (CCl_4) 1719 and 1679 cm^{-1}; NMR δ 1.00 (3 H, s), 1.09 (3 H, s), 1.17 (3 H, s), 1.37 (3 H, s), 1.60 (3 H, q, J = 1.1 Hz), 1.68 (3 H, q, J = 1.1 Hz), 2.88 (1 H, dd, J = 8.2, 0.80 Hz), 3.03 (1 H, d, J = 8.2 Hz), 6.61 (1 H, d, J = 10.2 Hz), 6.69 (1 H, dd, J = 10.2, 0.80 Hz); UV max (cyclohexane) 220 nm (log ϵ 3.92), 302 (1.76); mass spectrum, *m/e* (rel intensity) 286 (37), 216 (33), 201 (21), 178 (77), 163 (21), 150 (20), 135 (57), 134 (100), 119 (70), 105 (16), 91 (25), 82 (53), 78 (15), 41 (28).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.48; H, 7.75. Found: C, 75.39; H, 7.58.

4,5-Benzo-1,8,9,10,12,12-hexamethyltricyclo[6.2.2.0^{2,7}]-dodeca-4,9-diene-3,6,11-trione (3). A solution of 5 g (0.028 mol) of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one[3] and 5 g (0.032 mol) of 1,4-naphthoquinone in 30 mL of toluene was stirred at reflux under nitrogen for 22 h. The reaction mixture was concentrated under vacuum to give a black semisolid, which was dissolved in 100 mL of ether and washed with water (2 × 50 mL). The ether layer, after being dried over Na_2SO_4, was concentrated on the rotary evaporator to give 7.0 g (74%) of **3**, which was recrystallized from 95% ethanol as colorless plates: mp 132–132.5 °C; IR (CCl_4) 1721 and 1685 cm^{-1}; NMR δ 0.95 (3 H, s), 0.98 (3 H, m), 1.12 (3 H, s), 1.15 (3 H, s), 1.40 (6 H, m), 2.96 (1 H, d, J = 8.0 Hz), 3.20 (1 H, d, J = 8.0 Hz), 7.47 (4 H, s); UV max (MeOH) 345 nm (log ϵ 2.62), 291 (3.20), and 240 (3.96); mass spectrum, *m/e* (rel intensity) 336 (17), 267 (9), 266 (43), 265 (15), 252 (12), 251 (61), 179 (19), 178 (88), 163 (27), 150 (30), 135 (41), 134 (28), 133 (13), 132 (63), 119 (23), 105 (25), 104 (100), 91 (20), 77 (21), 76 (37), 41 (27).

Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.55; H, 7.11.

1,8,9,10,12,12-Hexamethyl-3,6-dihydroxytricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6,9-tetraen-11-one (4). Enolization of 2. To a solution of 0.50 g (1.75 mmol) of **2** in 8 mL of tetrahydrofuran and 7 mL of methanol in an ice bath was added dropwise (10 min) a solution of 0.30 g (5.9 mmol) of sodium methoxide in 10 mL of methanol. The ice bath was removed, and the reaction mixture was stirred for an additional 15 min and then added slowly to 150 mL of acidic ice water (pH < 5). The precipitate was filtered by suction, washed with water, and air-dried. The resulting brown solid was purified by recrystallization from cyclohexane. A total of 0.44 g (88%) of **4** was obtained: mp 103–105 °C; IR ($CDCl_3$) 1705 and 3650 cm^{-1}; NMR δ 0.79 (3 H, s), 1.03 (3 H, s), 1.75 (3 H, m), 1.82 (3 H, m), 1.88 (6 H, s), 4.43 (1 H, m), 4.54 (1 H, m), 6.42 (2 H, s); UV max (MeOH) 305 nm (log ϵ 3.27) and 250 (3.43);

mass spectrum, m/e (rel intensity) 286 (11), 271 (8), 258 (4), 243 (5), 227 (1), 217 (19), 216 (100), 215 (6), 201 (15), 189 (4), 173 (7), 105 (2).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.48; H, 7.75. Found: C, 75.60; H, 7.81.

Oxidation of 4. A solution containing 100 mg (0.35 mmol) of **4** in 10 mL of acetone was cooled in an ice bath. One milliliter of Jones reagent was slowly added, the ice bath was removed, and the reaction was continued for 1.5 h at room temperature. One milliliter of water was then added dropwise, and the solution was stirred for 10 min. Excess water was added, and the product was extracted with methylene chloride. This solution was dried (Na_2SO_4) and concentrated in vacuo to give 65 mg (65%) of **6** as an oil: IR ($CDCl_3$) 1715 and 1655 cm^{-1}; NMR δ 0.90 (3 H, s), 1.00 (3 H, s), 1.73 (6 H, m), 1.77 (6 H, s), 6.40 (2 H, s); mass spectrum, m/e (rel intensity) 284 (1), 214 (10), 121 (33), 109 (73), 108 (63), 111 (10), 88 (75), 86 (99), 84 (100), 83 (40), 82 (30), 74 (36), 49 (99). The compound was difficult to purify and was not analyzed.

1,8,9,10,12,12-Hexamethyl-3,6-dimethoxytricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6,9-tetraen-11-one (5). To 0.31 g (1.08 mmol) of **4** and 1 g of sodium hydroxide in 7 mL of tetrahydrofuran and 8 mL of methanol in an ice bath was added dropwise a solution of 1 mL of dimethyl sulfate in 5 mL of methanol. After addition, the reaction mixture was warmed to room temperature and stirred for an additional 2 h. The mixture was neutralized with 10% sodium bicarbonate and extracted with methylene chloride. This solution was concentrated in vacuo to give a brown oil, which was purified by passage through a silica gel column to give 0.144 g (42%) of **5** as colorless crystals: mp 125–126 °C; IR (CCl_4) 2815, 1715, 1260, 1210, 1040, 1000, and 820 cm^{-1}; NMR (CCl_4) δ 0.66 (3 H, s), 0.93 (3 H, s), 1.68 (6 H, m), 1.73 (6 H, m), 3.58 (3 H, s), 3.61 (3 H, s), 6.45 (2 H, s); UV max (cyclohexane) 292 nm (log ϵ 3.56); mass spectrum, m/e (rel intensity) 314 (17), 245 (23), 244 (100), 229 (64), 228 (13).

Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33. Found: C, 76.39; H, 8.29.

4,5-Benzo-1,8,9,10,12,12-hexamethyl-3,6-dimethoxytricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9-tetraen-11-one (8). To a solution of 104 mg (0.31 mmol) of **3** in 10 mL of benzene and 2.5 mL of dimethylformamide in an ice-cooled bath under nitrogen was added 120 mg (5 mmol) of sodium hydride. The reaction solution turned brown within a few minutes. To the brown solution was added a solution of 1 mL of methyl iodide in 10 mL of benzene. The reaction mixture was kept at room temperature under nitrogen for 8 h. It was then reacidified with dilute hydrochloric acid and extracted with methylene chloride. The organic extract was concentrated in vacuo to give **8** as an oil, which was purified by passage through a silica gel column. A total of 85 mg (76%) was collected: mp 149–150 °C; IR (CCl_4) 1710 cm^{-1}; NMR δ 0.77 (3 H, s), 1.09 (3 H, s), 1.72 (3 H, m), 1.81 (3 H, m), 1.92 (6 H, s), 3.70 (3 H, s), 3.80 (3 H, s), 7.30 (2 H, m), 7.80 (2 H, m); mass spectrum, m/e (rel intensity) 369 (51), 349 (13), 295 (19), 294 (78), 280 (23), 279 (100), 213 (71), 178 (24), 147 (13), 57 (26), 43 (56), 42 (28), 41 (44).

Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.01; H, 7.70.

1,9,10,11,12,12-Hexamethyl-4,7-dihydroxytricyclo-[7.2.1.0^{3,8}]dodeca-3,5,7,10-tetraen-2-one (9). Isomerization of 2 with HBr. A solution of 0.50 g (1.75 mmol) of **2** in 8 mL of glacial acetic acid containing 0.5 mL of 48% hydrobromic acid was heated at reflux for 15 min. The solution was poured into 100 mL of ice water and extracted twice with 100 mL of methylene chloride. The organic extract was washed successively with water, 10% sodium carbonate, and water again until neutral. The solution was dried (Na_2SO_4) and evaporated in vacuo to give an oil which was purified by passage through a Florisil column with methylene chloride to afford 0.4 g (78%) of **9**: mp 147–148 °C (recrystallized from cyclohexane); IR (CCl_4) 3620, 3450, and 1640 cm^{-1}; ^1H NMR (180 MHz) δ 0.93 (3 H, s), 1.00 (3 H, s), 1.13 (3 H, s), 1.46 (3 H, q, J = 1.2 Hz), 1.63 (3 H, q, J = 1.2 Hz), 1.66 (3 H, s), 4.13 (1 H, s), 6.65 (1 H, d, J = 8.5 Hz), 6.72 (1 H, d, J = 8.5 Hz), 12.44 (1 H, s); ^{13}C NMR δ 205.28, 157.69, 147.69, 145.24, 131.19, 126.50, 117.67, 114.89, 66.01, 58.08, 56.85, 21.62, 18.20, 14.80, 11.86, 10.02, 9.58; UV max (cyclohexane) 357 nm (log ϵ 2.68) and 256 (2.57); mass spectrum, m/e (rel intensity) 286 (8), 271 (27), 85 (23), 84 (100), 83 (19), 69 (97), 56 (99), 55 (99).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.48; H, 7.75. Found: C, 75.49; H, 7.85.

Methylation of 9 with Me_2SO_4. To a solution of 400 mg (1.40 mmol) of **9** and 1 g of sodium methoxide in 20 mL of methanol at 0 °C was added 2 mL of dimethyl sulfate. The reaction mixture was kept at 0 °C for 1.5 h, acidified with excess aqueous HCl, and extracted with methylene chloride. The methylene chloride solution was dried (Na_2SO_4) and evaporated to give a brown oil which, on TLC, indicated the formation of yellow product (**10**) (R_f 0.22 with methylene chloride). Thick layer chromatography afforded 299 mg (71%) of **10** as a pale yellow liquid: IR (CCl_4) 1645, 1475, 1450, 1330, 1250, 1185, 1000, 935 cm^{-1}; NMR δ 0.88 (3 H, s), 0.97 (3 H, s), 1.10 (3 H, s), 1.40 (3 H, m), 1.50 (3 H, s), 1.55 (3 H, m), 3.63 (3 H, s), 6.56 (1 H, d, J = 9 Hz), 6.87 (1 H, d, J = 9 Hz), 12.2 (1 H, s); mass spectrum, m/e (rel intensity) 300 (12), 285 (38), 96 (56), 95 (100), 86 (31), 84 (47), 69 (12), 56 (31), 55 (12), 45 (39); high-resolution mass spectrum, calcd for $C_{19}H_{24}O_3$ 300.17250, found 300.17254.

Dimethylation of 9. To a solution of **9** (286 mg, 1 mmol) in 20 mL of dimethylformamide at 0 °C under nitrogen was added 240 mg (10 mmol) of sodium hydride. Within a few minutes the solution became brown. A solution of methyl iodide (2 mL) in benzene (10 mL) was added. The mixture was allowed to warm to room temperature, kept for 2 h, and then acidified with dilute hydrochloric acid and extracted with methylene chloride. Evaporation of the solvent under vacuum gave a pale yellow solid which was recrystallized from petroleum ether (30–60 °C) to give 250 mg (80%) of **11**: mp 111–112 °C; IR (CCl_4) 1690, 1475, 1440, 1260, 1190, 1055, 985 cm^{-1}; NMR δ 0.90 (3 H, s), 0.97 (3 H, s), 1.09 (3 H, s), 1.40 (3 H, m), 1.53 (6 H, m), 3.64 (3 H, s), 3.73 (3 H, s), 6.70 (1 H, s), 6.77 (1 H, s); mass spectrum, m/e (rel intensity) 314 (trace), 271 (5), 269 (5), 231 (8), 229 (13), 227 (8), 219 (20), 217 (7), 205 (8), 203 (20), 201 (32), 199 (20), 178 (37), 166 (77), 163 (47), 147 (60), 145 (60), 121 (98), 119 (99), 117 (100), 94 (99), 93 (90).

Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33. Found: C, 76.42; H, 8.38.

Trimethylsilylation of 9. To a solution of trimethylsilyl chloride (1.0 mL) and trimethylamine (2.0 mL) in dimethylformamide (30 mL) cooled to −10 °C was added a solution of **9** (286 mg, 1 mmol) in the same solvent (10 mL). The mixture was gradually warmed to room temperature, stirred for 2 h, and then carefully poured into water (500 mL). Filtration gave a pale yellow solid which was washed with water (100 mL) and recrystallized from petroleum ether (30–60 °C) to give 323 mg (72%) of **13** as pale yellow crystals: mp 100–102 °C; NMR δ 0.17 (9 H, s), 0.27 (9 H, s), 0.83 (3 H, s), 0.91 (3 H, s), 1.04 (3 H, s), 1.37 (3 H, m), 1.47 (3 H, s), 1.50 (3 H, m), 6.33 (1 H, d, J = 9 Hz), 6.50 (1 H, d, J = 9 Hz); mass spectrum, m/e (rel intensity) 430 (3), 415 (8), 319 (3), 271 (3), 147 (3), 119 (2), 105 (2), 97 (2), 95 (4), 91 (3), 81 (4), 79 (3), 75 (16), 74 (13), 73 (100), 53 (4), 45 (30), 43 (16), 41 (19); high-resolution mass spectrum, calcd for $C_{24}H_{38}O_3Si_2$ 430.23591, found 430.23717.

Thin-layer chromatography of **13** (silica gel, CH_2Cl_2 eluent) gave instead the monosilyl derivative **14** as yellow crystals: mp 82–86 °C; IR (CCl_4) 1650, 1475, 1250, 1010 cm^{-1}; NMR δ 0.42 (9 H, s), 1.02 (3 H, s), 1.12 (3 H, s), 1.25 (3 H, s), 1.58 (3 H, m), 1.65 (3 H, s), 1.70 (3 H, m), 6.60 (1 H, d, J = 9 Hz), 6.82 (1 H, d, J = 9 Hz), 12.03 (1 H, s); mass spectrum, m/e (rel intensity) 358 (57), 343 (100), 286 (24), 271 (77), 263 (17), 147 (99), 148 (60), 73 (77); high-resolution mass spectrum, calcd for $C_{21}H_{30}O_3Si$ 358.19638, found 358.19623.

Isomerization of 5 with CF_3CO_2H. A solution of 72 mg (0.23 mmol) of **5** in 5 mL of trifluoroacetic acid was refluxed for 3.5 h. The reaction mixture was neutralized with aqueous sodium acetate and extracted with methylene chloride. Evaporation of the solvent gave light brown crystals which were separated by TLC into two components, 17 mg (24%) of **11** and 47 mg (66%) of **12**. Compound **11** agreed in melting point, mixture melting point, and NMR spectrum with the dimethylation product of **9** (vide supra). For **12**: mp 138.5–139.5 °C; IR (CCl_4) 1675, 1500, 1265, 1060 cm^{-1}; NMR δ 0.93 (6 H, s), 1.47 (3 H, m), 1.51 (3 H, s), 1.60 (3 H, m), 1.91 (3 H, m), 3.60 (3 H, s), 3.68 (3 H, s), 6.48 (2 H, s); mass spectrum, m/e (rel intensity) 314 (100), 299 (67), 286 (17), 271 (43), 265 (28), 241 (13), 240 (13), 225 (13), 219 (14), 217 (29), 197 (13).

Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33. Found: C, 76.55; H, 8.31.

Isomerization of 4 with CF_3CO_2H. A solution of 150 mg (0.53 mmol) of **4** in 10 mL of trifluoroacetic acid was heated at reflux for 2.5 h. The solution was diluted with 50 mL of water, neutralized by addition of saturated aqueous sodium bicarbonate, and extracted with methylene chloride. The organic layer was dried (Na_2SO_4) and concentrated in vacuo. The remaining oil had only one component, R_f 0.22 with methylene chloride, in accordance with **9**. The oil was purified by TLC (methylene chloride) to give 79 mg (53%) of **9**, mp and mmp 147–148 °C. Its NMR spectrum was identical with that of **9** obtained directly from **2**.

Isomerization of 8. (A) In Refluxing CF_3CO_2H. A solution of 81.5 mg (0.22 mmol) of **8** in 5 mL of trifluoroacetic acid was heated at reflux for 2 h. The reaction mixture was neutralized with aqueous sodium bicarbonate and extracted with chloroform. Evaporation of the solvent left a light brown solid, **24**, which was purified by TLC. A total of 25 mg (31%) was obtained: mp 161–162.5 °C; IR (CCl_4) 1620 cm^{-1} (H-bonded carbonyl); NMR δ 0.92 (3 H, s), 1.00 (3 H, s), 1.15 (3 H, s), 1.45 (3 H, m), 1.57 (3 H, m), 1.67 (3 H, s), 3.70 (3 H, s), 7.2 (2 H, m), 7.9 (2 H, m), 13.9 (1 H, s); mass spectrum, m/e (rel intensity) 350 (100), 335 (87), 291 (21), 281 (18), 150 (17), 91 (16), 57 (25), 55 (21), 43 (25), 41 (31).

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.60; H, 7.51.

(B) In CF_3CO_2H at Ambient Temperature. A solution of 15 mg of **8** in 0.4 mL of trifluoroacetic acid in an NMR tube was kept at room temperature (~25 °C) and the reaction was monitored by NMR. Reaction was almost complete in 1.5 h; the NMR spectrum indicated that the mixture was composed of 7% of the starting **8** and 86% of **23**; the rest consisted of unknown minor products. The reaction mixture was worked up in a manner similar to run A to give 10 mg (67%) of colorless crystals of 5,6-benzo-1,9,10,11,12,12-hexamethyl-4,7-dimethoxy-3,5,7,10-tetraen-2-one (**23**): mp 128–129.5 °C; IR (CCl_4) 1680 cm^{-1}; NMR δ 0.92 (3 H, s), 1.00 (3 H, s), 1.14 (3 H, s), 1.43 (3 H, m), 1.53 (3 H, m), 1.68 (3 H, s), 3.74 (3 H, s), 3.80 (3 H, s), 7.3 (2 H, m), 8.0 (2 H, m); mass spectrum, m/e (rel intensity) 364 (84), 349 (100), 269 (35), 152 (6), 105 (6), 91 (8), 86 (7), 84 (12), 72 (29), 71 (23), 70 (14), 57 (62), 56 (26), 55 (23), 44 (35), 43 (89).

Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.04; H, 7.77.

A solution of 10 mg of **23** in 0.3 mL of trifluoroacetic acid was heated at reflux for 2 h. An NMR spectrum indicated that 30% of **24** and 30% of the starting **23** were present in the reaction mixture, together with unidentified products.

Irradiation of 2. A solution of 0.5 g (1.75 mmol) of **2** in 120 mL of methylene chloride was irradiated with a 450-W water-cooled mercury arc lamp (Hanovia) with a Pyrex filter for 20 min until the original yellow color of the solution had disappeared. The photolysate mixture was concentrated in vacuo to give a colorless gummy solid. Preparative TLC (silica gel) with methylene chloride as the eluent gave **26** and **25** in isolated yields of 35% and 60%, respectively. 1,8,9,9,11,12-Hexamethyltetracyclo[6.3.1.$0^{2,7}$.$0^{11,12}$]dodec-4-ene-3,6,10-trione (**26**): mp >200 °C dec; IR (CCl_4) 1715 and 1675 cm^{-1}; NMR δ 0.75 (3 H, s), 1.08 (3 H, s), 1.12 (3 H, s), 1.15 (3 H, s), 1.21 (3 H, s), 1.30 (3 H, s), 2.57 (1 H, m), 3.10 (1 H, m), 5.95 (1 H, d, J = 5 Hz), 7.28 (1 H, d, J = 5 Hz); mass spectrum, m/e (rel intensity) 286 (6), 271 (1), 258 (1), 243 (1), 216 (12), 201 (12), 178 (54), 163 (45), 150 (37), 147 (43), 136 (11), 135 (99), 134 (100), 120 (14), 119 (59), 117 (13), 116 (13), 110 (30), 107 (23), 105 (35).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.48; H, 7.75. Found: C, 75.52; H, 7.87.

1,2,5,6,6,8-Hexamethylpentacyclo[8.2.0.$0^{4,9}$.$0^{5,11}$.$0^{8,12}$]dodecane-3,7,10-trione (**25**): mp >250 °C (colorless needles); IR (CCl_4) 1760, 1737, and 1708 cm^{-1}; NMR (CCl_4) δ 0.85 (6 H, s), 1.06 (3 H, s), 1.13 (6 H, s), 1.32 (3 H, s), 2.43 (4 H, s); UV max (MeOH) 302 nm (log ϵ 1.90); mass spectrum, m/e (rel intensity) 286 (17), 271 (2), 258 (2), 243 (11), 216 (25), 201 (18), 187 (2), 178 (33), 173 (12), 172 (10), 163 (10), 150 (13), 145 (8), 135 (34), 134 (100), 119 (25), 105 (12).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.48; H, 7.75. Found: C, 75.35; H, 7.56.

Irradiation of 0.10 g (0.35 mmol) of **2** in several solvents (130 mL) was performed under conditions similar to those of the above run. After 20 min of irradiation, the photolysates were concentrated in vacuo and analyzed by NMR without isolation. The results are given in the text.

Irradiation of 3. A solution of 0.10 g (0.35 mmol) of **3** in 120 mL of cyclohexane was irradiated with a 450-W water-cooled mercury arc lamp (Hanovia) with a Pyrex filter for 30 min. Examination of the reaction mixture by TLC indicated the formation of two components. One of them (R_f 0.17) was isolated and characterized as 4,5-benzo-1,8,9,9,11,12-hexamethyltetracyclo[6.3.1.$0^{2,7}$.$0^{11,12}$]dodec-4-ene-3,6,10-trione (**27**). A total of 31 mg (31%) was obtained: mp 148–149 °C; IR (CCl_4) 1720, 1690, 1610, 1380, 1290, 1140, 1030, 1020, 995 cm^{-1}; NMR δ 0.69 (3 H, s), 0.92 (3 H, s), 1.06 (3 H, s), 1.15 (3 H, s), 1.18 (3 H, s), 1.24 (3 H, s), 2.57 (1 H, m), 3.06 (1 H, m), 7.5 (4 H, m); mass spectrum, m/e (rel intensity) 336 (7), 321 (2), 308 (4), 293 (4), 267 (12), 266 (59), 265 (19), 252 (13), 251 (67), 224 (19), 223 (19), 179 (25), 178 (94), 163 (25), 160 (13), 150 (31), 149 (25), 135 (28), 134 (32), 132 (80), 105 (27), 104 (100), 91 (19), 76 (35), 43 (42).

Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.51; H, 7.13.

The lower spot (R_f 0.05) was eluted as a brown liquid, but the amount was too small to characterize.

Irradiation of 5. A solution of 61 mg (0.19 mmol) of **5** in 120 mL of cyclohexane was irradiated with a quartz-filtered mercury arc lamp for 50 min under nitrogen. Separation of the concentrated reaction mixture by TLC afforded 19.3 mg (41%) of crude 1,2,3,4-tetramethyl-5,8-dimethoxynaphthalene (**28**) as yellow solid. This solid still contained some impurities even after additional purification by TLC: NMR δ 2.28 (6 H, s), 2.60 (6 H, s), 3.72 (6 H, s), 6.37 (2 H, s).

Irradiation of 8. A solution of 16.2 mg (0.044 mmol) of **8** in 10 mL of cyclohexane was irradiated with a quartz-filtered mercury arc lamp under nitrogen. Separation of the concentrated reaction mixture by TLC gave 8 mg (61%) of 1,2,3,4-tetramethyl-9,10-dimethoxyanthracene (**29**), which was characterized only by NMR, though it was not pure; NMR δ 2.36 (6 H, s), 2.80 (6 H, s), 3.7 (6 H, s), 8.0 (4 H, m).

Reaction of 3 with CH_3ONa. (A) Under Nitrogen. A solution of 202 mg (0.60 mmol) of **3** in 20 mL of methanol was saturated with nitrogen prior to and during the following reaction. To the methanol solution was added 0.3 g of sodium methoxide in 10 mL of methanol at 0 °C under a nitrogen atmosphere. With addition of the sodium methoxide solution, the color of the reaction gradually changed to dark brown. The solution was stirred for 2 h in an ice bath. The reaction mixture was then poured into excess dilute hydrochloric acid, extracted with methylene chloride, and dried (Na_2SO_4). The yellow material which remained after concentration in vacuo was identified to be **3** (200 mg, 99%) by its NMR spectrum.

(B) Under Air. To a solution of 221 mg (0.66 mmol) of **3** in 10 mL of methanol cooled to 0 °C was added 200 mg of sodium methoxide in 10 mL of methanol under air. Stirring was continued for 1 h at 0 °C, and the mixture was kept for an additional 2 h at room temperature. The reaction mixture was poured into excess dilute hydrochloric acid, and the resulting precipitate was filtered (189 mg). The solid was washed with ether. Undissolved solid was recrystallized from cyclohexane and characterized as 1,2,3,4-tetramethylanthraquinone (**31**), yellow needles (8 mg, 5%): mp 236–236.5 °C; NMR δ 2.65 (6 H, s), 2.33 (6 H, s), 7.5 (2 H, m), 7.8 (2 H, m); mass spectrum, m/e (rel intensity) 264 (100), 249 (22), 235 (5), 221 (43), 178 (14), 165 (8), 124 (8), 91 (21), 77 (9), 44 (25).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.69; H, 6.07.

The filtrate was concentrated in vacuo to give a pale yellow viscous oil (180 mg, 78%), which solidified on standing. Recrystallization from cyclohexane afforded colorless crystals (**30**): mp 108–110 °C; NMR δ 0.92 (3 H, s), 1.03 (3 H, s), 1.67 (3 H, m), 1.77 (3 H, m), 1.80 (6 H, s), 7.5 (4 H, m); IR (CCl_4) 1725, 1700, 1285, 875 cm^{-1}; UV max (methanol) 350 nm (log ϵ 2.49), 302 (3.22); mass spectrum, m/e (rel intensity) 350 (97), 335 (40), 307 (40), 291 (21), 289 (22), 280 (59), 279 (33), 266 (26), 265 (100), 264 (99), 263 (99), 262 (20), 261 (37), 252 (54), 238 (59), 219 (31), 178 (39), 165 (34), 115 (36), 105 (43), 104 (42).

Anal. Calcd for $C_{22}H_{22}O_4$: C, 74.97; H, 6.86. Found: C, 75.38; H, 6.43.

(C) With H_2O_2 under N_2. To the deep red solution of 205 mg (0.61 mmol) of **3** in 15 mL of methanol made by addition of 200 mg of sodium methoxide under nitrogen was added dropwise 1 mL of 30% hydrogen peroxide with stirring for 15 min at 0 °C. The solution was warmed to room temperature and stirred for an additional 15 min under nitrogen. The solution was then poured into excess dilute hydrochloric acid, extracted with methylene chloride, dried (Na_2SO_4), and evaporated to give a colorless viscous liquid. An NMR spectrum shows that the oil was a mixture of 24% of **30** and 76% of the starting **3**.

Epoxidation of 2 with Alkaline H_2O_2. A solution of 1.00 g (3.5 mmol) of **2** and 1.02 mL (10 mmol) of 30% aqueous hydrogen peroxide in 20 mL of methanol was cooled to 10 °C, and 2 mL of 1 N sodium hydroxide was added dropwise with stirring over a period of 1 h. The mixture was maintained with stirring at 15–20 °C for 3 h and then diluted with 100 mL of water and one drop of dilute hydrochloric acid. Extraction with ether (3 × 30 mL) followed by evaporation of the solvent in vacuo gave a solid which when recrystallized from cyclohexane gave colorless crystals (**32**): mp 141.5–142.5 °C; NMR δ 0.93 (3 H, s), 1.05 (3 H, s), 1.38 (3 H, s), 1.45 (3 H, s), 1.67 (3 H, m), 1.80 (3 H, m), 3.20 (1 H, d, J = 12 Hz), 3.60 (2 H, s), 3.62 (1 H, d, J = 12 Hz); UV max (methanol) 299 nm (log ϵ 2.48); mass spectrum, m/e (rel intensity) 302 (17), 232 (27), 178 (11), 174 (16), 161 (32), 135 (18), 134 (55), 119 (28), 91 (13), 79 (11), 58 (80), 43 (100), 41 (25).

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.74. Found: C, 71.01; H, 7.35.

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Liquid-Phase Catalytic Hydrogenation of 1,4-Cyclohexanedione: Activity and Selectivity

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Liquid-phase catalytic hydrogenation of 1,4-cyclohexanedione was carried out by using various metal catalysts on SiO_2 (Ni, Cu, Pd, Pt, Ir, Ru) in 2-propanol as solvent under low hydrogen pressure, 6.2 bar, and 20 °C. A kinetically consecutive process, diketone → ketol → diol, is obtained, and 4-hydroxycyclohexanone may be obtained in a single step at a yield of 70% by utilizing Ru/SiO_2. The rate and the selectivity for the first step of the reaction giving the ketol were examined as a function of several parameters: hydrogen pressure, substrate concentration, and temperature. The kinetic orders are 1 in H_2 and −0.6 in diketone with an activation energy of 11 kcal/mol.

One of the main objectives of chemistry is to devise and improve methods which allow the selective reaction of only one of the functional groups in a bifunctional molecule.

Our interest in this area is in the selective reduction of 1,4-cyclohexanedione to its corresponding ketol, 4-hydroxycyclohexanone. We chose to examine this ketone since its conformation has been definitively established as the twist-boat in the liquid phase.[1-4] This structure allows us to disregard the existence of the enol form and suggests a simultaneous adsorption of the two carbonyls on the surface of the catalyst.

The catalytic hydrogenation was carried out in the liquid phase by using a hydroxylic solvent, 2-propanol or water. The metal used was generally ruthenium, since this catalyst has often been utilized for the hydrogenation of ketones, as reported by Augustine,[5] Rylander,[6] and Freifelder.[7] However, other metals such as platinum, iridium, and copper were also examined and compared.

In this work, we report on (1) the rate of disappearance of the diketone as a function of several parameters such as the hydrogen pressure, the amount of substrate, the temperature, the amount of catalyst, and the nature of the metal and (2) the selectivity of the reaction, which is defined by the ratio of the number of moles of product ketol to the total number of moles of ketol plus diol.

Experimental Section

Apparatus. Two different types of apparatus were used: an apparatus for the work at hydrogen pressures less than 1 bar[8] and one for higher pressures, an autoclave (Autoclave Engineers type Magnedrive) with a capacity of 0.3 L, which allowed the removal of samples without stopping the agitation.

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