systems. Equations used in the manual calculations were as follows:[3c]

above T_c (where $1/\tau^* \gg 2\pi\Delta\nu$): $1/\tau^* = \pi(\Delta\nu)^2(W^* - W')^{-1}$ (1)

at T_c: $1/\tau^* = \sqrt{2}\pi\Delta\nu$ (2)

below T_c (where $1/\tau^* \ll 2\pi\nu$): $1/\tau^* = 2\pi(W^* - W')$ (3)

where W^* and W' are the line widths in the presence and absence of exchange, respectively; the line width of the 4-methoxy group peak was used for W'. At each temperature the rate constant, k, was determined and a least-squares plot of ln k vs. $1/T$ yielded the Arrhenius activation energy, E_a. Values for $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ were obtained from the appropriate equations.[3b] Alternately, $\Delta G^{\ddagger}$ was obtained from the Gutowsky–Holm approximation[6] (eq 2 above) and Eyring[3b] equation at the coalescence temperature. Errors were determined by a propagation of errors treatment.

Registry No.—1, 37706-47-1; 2, 61770-02-3; 3, 37706-46-0; 4, 37706-35-7; (*N*-(2-benz[*h*]quinolylmethyl)-3,5-dimethoxybenzamide, 61770-03-4.

References and Notes

(1) Taken in part from the Ph.D. Dissertations of J. C. Schmidt and H. D. Benson, University of Cincinnati, 1976 and 1972, respectively.

(2) H. Zimmer and H. D. Benson, *Chimia*, **26**, 131 (1972).

(3) (a) For a discussion of conformational rate processes determined by NMR, see K. C. Ramey, D. C. Lini, and G. Krow, *Annu. Rep. NMR Spectrosc.*, **6a**, 160 (1975); (b) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968); (c) A. L. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966); (d) S. Gladstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941.

(4) Peak assignments were made by comparison with known compounds containing the trimethoxyphenyl moiety.

(5) The absorptions for the 2 and 6 protons of the phenyl ring at low temperatures exhibited a $\Delta\nu$ of 181 Hz. It follows from the Gutowsky–Holm approximation (eq 2 in Experimental Section, see also ref 6) that the coalescence temperature should in this case be higher by about 5 °C, but this was not rigorously checked.

(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(7) J. T. D'Agostino, Ph.D. Dissertation, University of Cincinnati, 1969.

(8) R. S. Macomber, *J. Chem. Educ.*, **53**, 279 (1976).

(9) G. Binsch, *J. Am. Chem. Soc.*, **91**, 1304 (1969).

(10) Assignments of the 2 and 6 protons were deduced from coupling considerations at temperatures below T_c.

(11) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, N.Y., 1972, p 303.

Unusual Effect of Epoxidic Oxygen on the Ease of Base-Catalyzed Decomposition of Epidioxides

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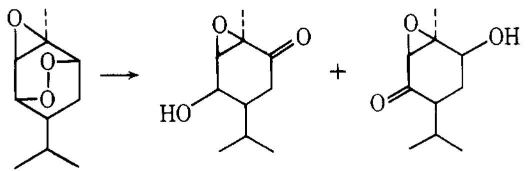
Department of Chemistry, The Florida State University, Tallahassee, Florida 32306

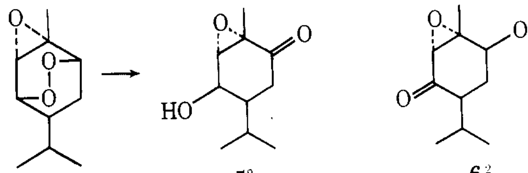
Received October 15, 1976

In a parallel study[2] we observed that attempts to separate a mixture of 1 and 2 by column chromatography or preparative TLC over silica gel resulted in rapid destruction of only one of the components, namely **1**. This peculiar selectivity attracted our attention and the reaction was examined in more detail.

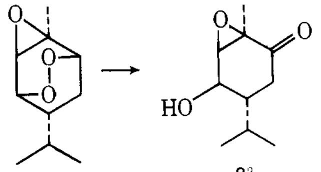
Pure **1**, isolated by *rapid* preparative TLC followed by recrystallization, was stirred overnight with silica gel. TLC analysis indicated complete conversion to two new substances which were isolated by preparative TLC in 58 and 30% yield. Both compounds were isomeric hydroxy ketones (IR spectrum) which were differentiated by NMR spectrometry. The NMR spectrum of the major product **3** exhibited a somewhat broadened triplet at 4.28 ppm (J = 4.5 Hz, H-3) which was clearly coupled to a doublet at 3.66 ppm (H-2), whereas the minor product **4** had a triplet at 4.06 ppm (J = 7.5 Hz, 6) and a singlet at 3.12 ppm (H-2). Under these conditions **2** underwent no significant change, but prolonged stirring with silica gel (5 days) resulted in 51% recovery of **2** and 44% conversion to the known[2] γ-hydroxy-α-epoxy ketone **5**. There was no evidence for formation of the isomeric hydroxy ketone **6**.[2]



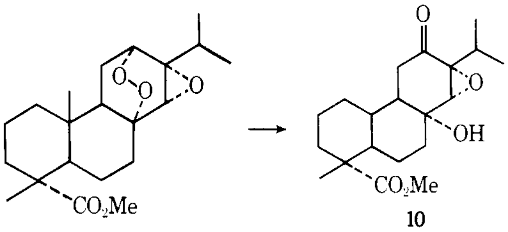
1[2] **3** **4**



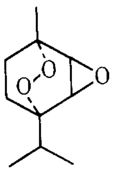
2[2] **5**[2] **6**[2]



7[2] **8**[2]



9 **10**



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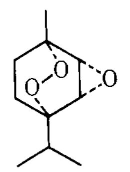

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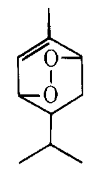
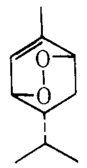


13[2]

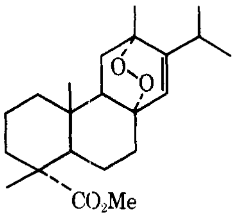


14[2]

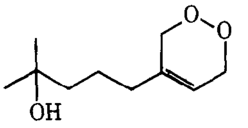
The two cis epoxy epidioxides **7**[2] and **9**[5] also underwent essentially quantitative conversion to the γ-hydroxy-α-epoxy ketones **8** and **10** on stirring overnight with silica gel. On the other hand, neither **11** nor **12**, prepared by epoxidation of ascaridole in 48 and 32% yield, respectively, was affected by this procedure. The stereochemistry assigned to **11** and **12** is tentative; the minor, more polar isomer exhibited the signals of H-2 and H-3 as an AB system centered at 3.25 ppm (J = 5 Hz), whereas H-2 and H-3 of the major, less polar isomer were a two-proton singlet at 3.31 ppm. The same relationship of chemical shifts and polarities is characteristic of the cis and trans epoxy peroxides **1**[2] and **2**[2] and the cis and trans epoxy peroxides **21** and **22** (vide infra); however, formation of **11** in somewhat larger amount by attack from what appears to be the more hindered side seems surprising.

The 3,6-dihydro-1,2-dioxins **13**–**18**[2,7-9] were also stable toward silica gel[10] as were the mixtures of α- and β-epoxides **19** and **20** prepared by epoxidation of **16** and **17**.[8] Consequently the facile decomposition of epidioxides under the influence of silica gel depends on two factors: (1) the presence of a proton α to the epidioxide groups, presumably so that decomposition can take place by a process resembling the usual base-catalyzed decomposition of peroxides;[4] (2) the presence of a rigid system in which an epoxidic oxygen is situated cis and in close proximity to the epidioxide function.[12]

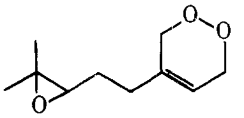
The reasons for the unusually facile decomposition of the



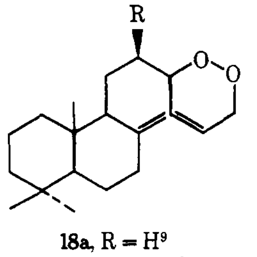
15[7]



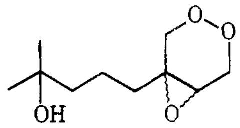
16[8]



17[8]



18a, R = H[9]
b, R = OH[9]



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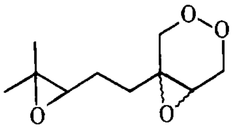

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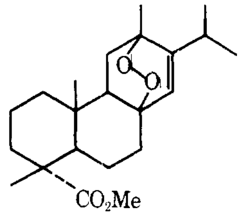
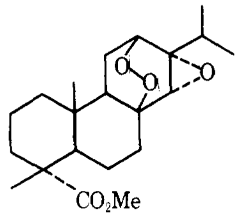


21[13]



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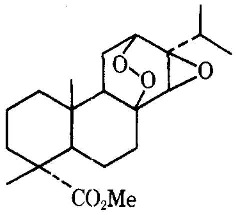
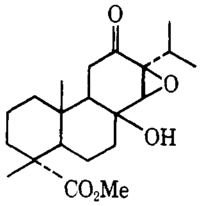
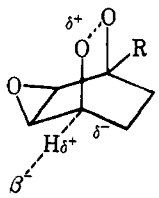


23



24

cis epoxy peroxides are obscure. One possibility is that transition state I in which one of the peroxidic oxygens must assume a partial positive charge is somehow stabilized by the epoxidic oxygen atom in the cis epoxide. Alternatively, the more polar cis epoxides might be more efficiently adsorbed on silica gel than the less polar trans epoxides and hence would be decomposed much more readily.



I

The generalizations presented in the preceding discussion provided a basis for assigning the correct stereochemistry to two substances obtained in approximately equal amounts by epoxidation of **21**.[13] The NMR spectrum of the crude reaction product revealed the presence of two isomers **22** and **23** (two H-14 singlets at 3.04 and 3.09 ppm).[14] Attempts to separate the mixture by preparative TLC resulted in isolation of a less polar epoxidic epidioxide (IR band at 1715 cm^{-1}; NMR singlet at 3.09 and multiplet at 4.37 ppm) and isolation of a more polar γ-hydroxy-α-keto epoxide (IR bands at 3500, 1720, and 1710 cm^{-1}; NMR singlet at 3.16 ppm). The hydroxy ketone must have been formed by rearrangement of **23**; hence its stereochemistry is represented by formula **24** and that of the unrearranged epoxy epidioxide is **22**.

Experimental Section[15]

Epoxidation of Ascaridole. A solution of 0.375 g of ascaridole and 500 mg of *m*-chloroperbenzoic acid in 20 mL of $CHCl_3$ was stirred for 10 days. The solution was washed thoroughly, dried, and evaporated and the two products were separated by preparative TLC (solvent 1:1 ether–hexane). The less polar epoxy peroxides,[11] wt 195 mg (48%), was repurified by preparative TLC and cyrstallized on drying: mp 42–44 °C; NMR signals at 3.31 (2 protons, H-2 and H-3), 1.31 (C-1 methyl), 1.01 d and 0.96 ppm d (J = 7 Hz, isopropyl methyls).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.00; H, 8.84.

The more polar product **12**, wt 133 mg (32%), was a gum which had NMR signals at 3.25 (center of AB system, J_{AB} = 5 Hz, H-2 and H-3), 1.30 (C-1 methyl), and 1.02 ppm d (J = 7 Hz, isopropyl methyls). The analytical sample was repurified by preparative TLC.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.91; H, 8.57.

Epoxidation of 16. A solution of 1.08 g of **16**[8] and 1.3 g of *m*-chloroperbenzoic acid in 20 mL of $CHCl_3$ was stirred for 20 h and worked up as in the preceding section. This gave 1.02 g (93%) of gummy **19** (mixture of α- and β-epoxides) which was purified by preparative TLC (no indication of decomposition on the plate) and had an IR band at 3400 cm^{-1}; NMR signals at 4.33 d (J = 2 Hz, H-8), 4.24 (H-6a), 3.29+ (J = 2 Hz, H-7), and 1.20 ppm (two superimposed methyls).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.28; H, 9.12.

Reaction of this material with $FeSO_4\cdot7H_2O$ or $FeSO_4\cdot7H_2O$ and $Cu(OAc)_2$[2] gave a complex mixture of products.

Epoxidation of 17. A solution of 0.800 g of **17**[8] and 0.825 g of *m*-chloroperbenzoic acid in 25 mL of $CHCl_3$ was stirred overnight and worked up as usual. The gummy product, wt 0.804 g, presumably a mixture of epimers at C-3, C-6, and C-7, was further purified by TLC. There was no indication of decomposition on the plate. The material had NMR signals at 4.34 d (J = 2 Hz, H-8), 4.25 (H-9), 3.33 q (somewhat distorted, indicative of presence of a mixture, H-7), 2.70 tbr (J = 5 Hz, H-3), 1.28 and 1.25 ppm (two methyls).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.41; H, 8.19.

Epoxidation of 21. A solution of 0.120 g of **21**[13] and 90 mg of *m*-chloroperbenzoic acid in 20 mL of $CHCl_3$ was refluxed for 3 h and then stirred overnight. The usual workup yielded a gum which was subjected to preparative TLC (two elutions with 2:5 ether–hexane) and gave 45 mg (36%) of less polar **22** and 45 mg (36%) of more polar **24**. In a second run using 0.200 mg of **21**, 86 mg (41%) of **22** and 80 mg (38%) of **24** were isolated. The less polar **22** (methyl 8β,12β-epidioxy-13α,14α-epoxyabieten-18-oate) proved difficult to recrystallize but finally formed crystals, mp 98–99 °C, which were suitable for elemental analysis and had IR bands at 1715 and 1242 cm^{-1}; NMR signals (90 MHz) at 4.37 m (H-12), 3.63 (methoxyl), 3.06 (H-14), 1.18 (C-4 methyl), 1.11 (C-10 methyl), 1.03 d and 0.96 ppm d (J = 7 Hz, isopropyl methyls).

Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85; O, 21.95. Found: C, 69.24; H, 8.90; O, 21.60.

The more polar material **24** (methyl 13β,14β-epoxy-8β-hydroxy-12-oxoabietan-18-oate) was recrystallized from methanol-water: mp 161–162 °C; IR bands at 3500, 1720, 1710, and 1250 cm^{-1}; NMR signals (270 MHz) at 3.68 (methoxyl), 3.16 (H-14), 1.20 (C-4 methyl), 1.00 (C-10 methyl), 0.95 d and 0.86 ppm d (J = 7 Hz, isopropyl methyls).

Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85; O, 21.95. Found: C, 69.00; H, 8.97; O, 21.90.

Reactions of Epoxy Peroxides with Silica Gel. Solutions of the peroxides in the appropriate solvent were stirred with 2 g of silica gel (Merck $PF_{254+366}$). The mixture was filtered and the silica gel was washed thoroughly with warm solvent. The combined filtrate and washings were evaporated to dryness at reduced pressure. The residue was analyzed by TLC, separated by preparative TLC when necessary, isolated, and identified.

A. **1**[2] (0.200 g) in ether was stirred overnight and silica washed with warm $CHCl_3$. Preparative TLC of the residue (eluent 7:3 ether–hexane) gave 116 mg (58%) of **3** and 60 mg (30%) of **4**. There was no evidence of starting material. Hydroxy ketone **3** crystallized on drying: mp 89–90 °C; IR bands at 3490 and 1695 cm^{-1}; NMR signals at 4.28 tbr (J = 5 Hz, H-3), 3.66 d (J = 4.5 Hz, H-2), 1.39 (C-1 methyl), 1.00 d and 0.90 ppm d (J = 7 Hz, isopropyl methyls).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.44; H, 8.85.

The gummy hydroxy ketone **4** had IR bands at 3440 and 1702 cm^{-1}; NMR signals at 4.06 t (J = 7.5 Hz, H-6), 3.12 (H-2), 1.52 (C-1 methyl), 0.93 d and 0.83 ppm d (J = 6.5 Hz, isopropyl methyls). For analysis, the sample was purified once more by preparative TLC.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.05; H, 8.80.

B. 2[2] (0.200 g) under conditions A underwent no change. On stirring for 5 days, preparative TLC (1:1 hexane–ether) gave 51% of **2**, 44% of **5**.[2]

C. 7 (0.100 g) for 2 days, silica washed with warm $CHCl_3$, gave 94% of **8**.[2]

D. 9[5] (0.100 g) overnight, silica washed with warm $CHCl_3$, gave a 100% yield of **10**.[5]

E. 19[13] (0.100 g) for 2 weeks resulted in 99% recovery of starting material.

F. 20[13] (0.100 g), 2 weeks, preparative TLC of product resulted in quantitative recovery of starting material.

G. 11 (0.100 g), 2 days, gave 96% of starting material.

H. 12 (0.040 g), 2 days, gave 95% of starting material.

I. 16[13] (0.250 g), 2 weeks, gave quantitative recovery of starting material.

Registry No.—**1**, 61616-18-0; **2**, 61617-12-7; **3**, 61617-13-8; **4**, 61597-56-6; **5**, 61616-19-1; **7**, 61570-83-0; **8**, 61570-84-1; **9**, 25859-65-8; **10**, 34217-21-5; **11**, 61597-57-7; **12**, 61617-14-9; **16**, 57073-98-0; **17**, 56764-67-1; **19**, 61597-58-8; **20**, 61597-59-9; **21**, 5309-31-9; **22**, 61617-15-0; **24**, 61688-31-1; ascaridole, 512-85-6; $FeSO_4$, 19468-88-3.

References and Notes

(1) Supported in part by a grant from the National Science Foundation (GP-12582).

(2) J. A. Turner and W. Herz, *J. Org. Chem.*, **42**, 1895 (1977) (see footnote 9 of this reference).

(3) Column chromatography of **1** or **2** over Florisil or basic alumina (Alcoa F-20) resulted in decomposition of both isomers to hydroxy ketones, presumably by the Kornblum–De La Mare mechanism.[4]

(4) N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, **73**, 880 (1951).

(5) W. Herz and R. C. Ligon, *J. Org. Chem.*, **37**, 1400 (1972).

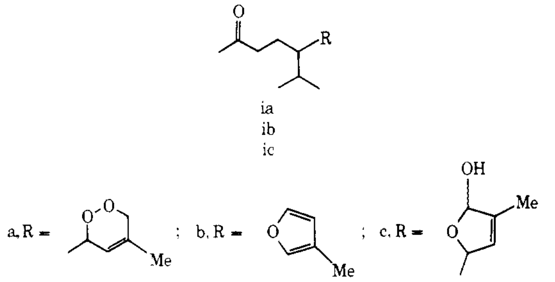
(6) G. O. Schenck, K. G. Kinkel, and W. J. Mertens, *Justus Liebigs Ann. Chem.*, **584**, 125 (1953); G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

(7) R. N. Moore and R. V. Lawrence, *J. Am. Chem. Soc.*, **80**, 1438 (1958).

(8) M. Matsumoto and K. Kondo, *J. Org. Chem.*, **40**, 2259 (1975).

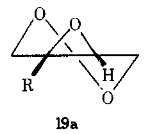
(9) J. A. Turner and W. Herz, *J. Org. Chem.*, **42**, 1900 (1977).

(10) Treatment of ia with basic alumina results in conversion to the hemiacetal ib which furnishes ic on chromatography over silica gel.[11] In our hands, column chromatography of **16–18** over silica gel yielded traces of the corresponding furans after several days' exposures, but preparative TLC over silica gel produced no change in the starting materials.

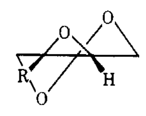


(11) E. Demole, C. Demole, and D. Berthot, *Helv. Chim. Acta*, **56**, 265 (1973).

(12) The most stable conformations of **19** and **20** are half-chair conformers **19a** and **19b** in which the O–O bond is not in the same relationship to the epoxide oxygen as in the cis epoxy dioxides **1**, **7**, **9**, and **22**.



19a



19b

(13) W. Herz, R. C. Ligon, J. A. Turner, and J. F. Blount, *J. Org. Chem.*, **42**, 1885 (1977).

(14) By contrast, epoxidation of **15** where attack from the "β face" is severely restricted furnished only one isomer, i.e., **9**.[5]

(15) Experimental details are given in ref 2 and 13.

3-Carbo-*tert*-butoxybenzene Oxide

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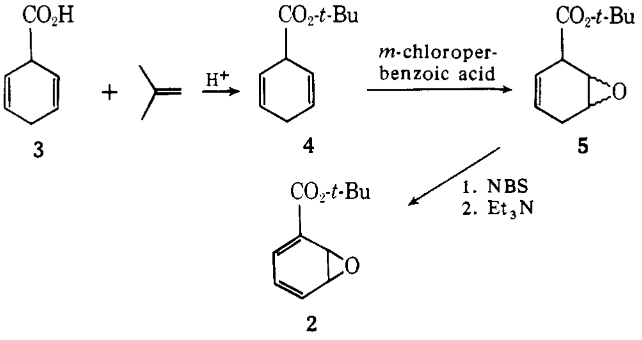
Received October 29, 1976

Since the initial synthesis of oxepin-benzene oxide was reported,[1] there has been considerable interest in the chemistry and biochemistry of arene oxides.[2-5] 4-Carbo-*tert*-butoxyoxepin-benzene oxide (**1**) has been prepared in these laboratories and, although **1** exists predominantly as the oxepin valence isomer,[6] nonetheless it reacts with nucleophiles at the 3 position of the benzene oxide valence isomer to afford *tert*-butyl trans-2-substituted 3-hydroxy-2,3-dihydrobenzoates.[6,7]

The synthesis of 3-carbo-*tert*-butoxybenzene oxide (**2**) was accomplished through a four-step procedure as indicated in Scheme I. Esterification of 1,4-dihydrobenzoic acid (**3**) with isobutylene and acid catalysis afforded **4** (65%) that was oxidized with *m*-chloroperbenzoic acid to give a 1:1 mixture of *cis*- and *trans*-**5** (67%). The isomers could be separated by preparative GLC but were used as a mixture for subsequent reactions. Allylic bromination of **5** followed by treatment with Et_3N afforded **2** as a bright yellow oil (35%).

Scheme I



The spectral data indicate that **2** exists as the benzene oxide valence isomer, but the color of **2** suggests that the oxepin valence isomer is present to a small extent. Benzene oxide **2** is aromatized with aqueous acid to a 1:1.7 mixture of *m*- and *o*-hydroxybenzoic acids, respectively. Whereas **1** reacts readily with nucleophiles,[6,7] attempts to effect nucleophilic addition to **2** with HO^-, CH_3O^-, N_3^-, and $C_6H_5S^-$ gave either no reaction or a complex mixture of products.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 237 spectrophotometer. Ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. ^1H NMR spectra, unless otherwise indicated, were taken on a Varian Model T-60 spectrometer, and chemical shift data are reported in parts per million downfield from tetramethylsilane as an internal standard at 0.00. Mass spectra were run on a Hitachi Perkin-Elmer RMU-6D mass spectrometer with an ionizing potential of 70 eV and are expressed in percent relative to the most intense peak. Except for the high mass region only the *m/e*'s of greater than 20% relative intensity are listed. Melting points were taken on a Thomas-Hoover "Uni-Melt" and are corrected. Gas chromatographic analyses were carried out with a Hewlett-Packard Model 5750 gas chromatograph with thermal conductivity detectors. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

***tert*-Butyl 1,4-Dihydrobenzoate (4).** Ester **4** was prepared in 65% yield from **3**[8] by the general procedure of McCloskey and Fonken:[9] bp 42–44 °C (0.2 Torr); IR (CCl_4) 3040, 1733, 1637, 1252, 1206 cm^{-1}; NMR (CCl_4) δ 1.45 (s, 9 H), 2.65 (d, 2 H, J = 9 Hz), 3.50 (t, 1 H, J = 9 Hz), 5.75 ppm (broad s, 4 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.11; H, 8.86.