dence 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]

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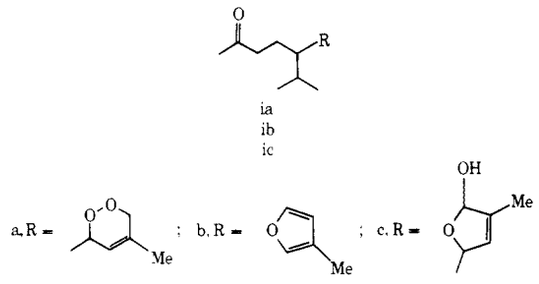
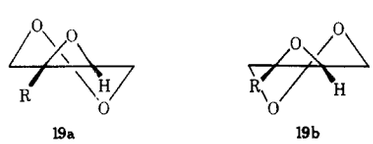
(9) J. A. Turner and W. Herz, *J. Org. Chem.*, **42**, 1900 (1977).

(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**.



(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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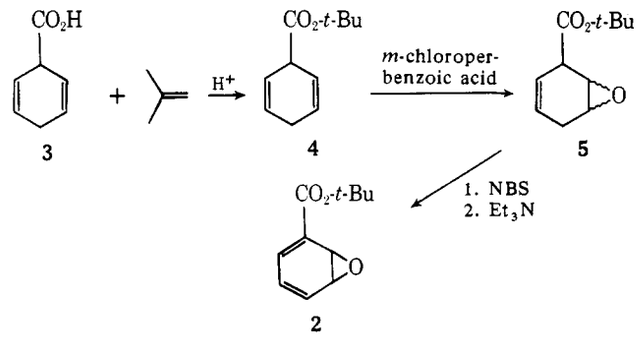
Since the initial synthesis of oxepin-benzene oxide was reported,[1] there has been considerable interest in the chemistry and biochemistry of arene oxides.[2-5] 4-Carbo-*tert*-butoxyoxepin-benzene oxide (**1**) has been prepared in these laboratories and, although **1** exists predominantly as the oxepin 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

Scheme I



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%).

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.

***cis*- and *trans-tert*-Butyl 2,3-Oxo-1,4-dihydrobenzoate (5).** To a stirring solution of 2.00 g (11.1 mmol) of **4** in 20 mL of CH_2Cl_2 at 0 °C was added a solution of 2.26 g (11.1 mmol) of 85% *m*-chloroperbenzoic acid in 30 mL of CH_2Cl_2. After the addition was complete (0.5 h), the solution was stirred at 0 °C for an additional 0.5 h after which it was warmed to room temperature and stirred for 17 h. The solution was washed with three 25-mL portions of saturated aqueous Na_2CO_3 and 25 mL of saturated aqueous NaCl and dried (K_2CO_3). Filtration and evaporation under vacuum gave 2.08 g of a pale yellow oil. Distillation gave, after a small forerun, 1.40 g (67%) of *cis*- and *trans*-**5** as a colorless oil, bp 55–57 °C (0.2 Torr). GLC analysis (6 ft × 0.25 in, 15% SE-30, 130 °C) of the distillate showed the presence of the two isomers in a ratio of 1:1 with retention times of 11.8 (A) and 14.2 min (B). Preparative GLC provided pure samples of both isomers.

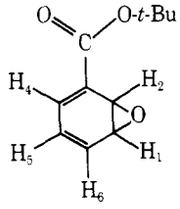
Isomer A: IR (CCl_4) 3055, 1730, 1370, 1288, 1258, 1150 cm^{-1}; NMR (CCl_4) δ 1.40 (s, 9 H), 2.4–2.6 (m, 2 H), 3.0–3.6 (m, 3 H), 5.4–5.6 ppm (m, 2 H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.06; H, 8.25.

Isomer B: IR (CCl_4) 3042, 1737, 1365, 1280, 1255, 1152 cm^{-1}; NMR (CCl_4) δ 1.50 (s, 9 H), 2.3–2.5 (m, 2 H), 3.0–3.6 (m, 3 H), 5.4–5.6 ppm (m, 2 H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.13; H, 8.30.

3-Carbo-*tert*-butoxybenzene Oxide (2). To a solution of 11.32 g (57.7 mmol) of *cis*- and *trans*-**5** in 100 mL of CCl_4 was added 12.30 g (69.2 mmol) of finely ground *N*-bromosuccinimide. The suspension was stirred under reflux and irradiated with an ultraviolet lamp until the bromination was complete. The mixture was cooled to room temperature, filtered, and evaporated under vacuum to give 15.6 g (98%) of allylic bromide as a viscous yellow oil. The crude bromide was dissolved in 100 mL of diethyl ether and 7.30 g (72.1 mmol) of triethylamine was added in one portion. A crystalline salt precipitated immediately. The mixture was filtered to remove the salt; the filtrate was diluted with 100 mL of diethyl ether and washed with three 150-mL portions of water followed by repeated washings with 200-mL portions of 5% aqueous NaOH until the aqueous wash was colorless. The ether solution was dried (K_2CO_3), filtered, and evaporated under reduced pressure to give 11.1 g of a dark, viscous oil. Distillation through a short-path still afforded 3.87 g (35%) of **2** as a bright yellow oil: bp 60–65 °C (]/]5 Torr); IR (CCl_4) 1708, 1670, 1628, 1365, 1280, 1160 cm^{-1}; UV max (CH_3OH) 286 nm (ε 3100); UV max (isooctane) 283 nm (ε 4100); mass spectrum *m/e* 194 (8), 177 (8), 162 (15), 138 (24), 123 (17), 121 (17), 105 (23), 104 (32), 57 (33), 56 (26), 55 (23), 44 (45), 43 (44), 41 (100); NMR (220 MHz, CCl_4).[10]



	δ, ppm	*J*, Hz
H_1	4.29	$J_{1,2}$ = 2.75; $J_{1,5}$ = 1.65; $J_{1,6}$ = 4
H_2	4.91	$J_{2,4}$ = 2
H_4	6.90	$J_{4,5}$ = 7.05; $J_{4,6}$ = 1.3
H_5	6.26	$J_{5,6}$ = 8.45
H_6	6.34	
$(CH_3)_3C$	1.59	

Benzene oxide **2** formed a 1:1 adduct in 65% yield with maleic anhydride in benzene. It was recrystallized from benzene as white flakes: mp 176–177 °C; IR ($CHCl_3$) 1860, 1790, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (s, 9 H), 3.3–3.9 (m, 5 H), 5.8–6.6 ppm (m, 2 H).

Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.90; H, 5.38.

Acid-Catalyzed Aromatization of 2. A solution of 100 mg of **2** in a mixture of 2 mL of CF_3CO_2H and 2 mL of water was stirred at room temperature. The solution was evaporated to dryness under reduced pressure, and the white, crystalline residue was dissolved in 1 mL of acetone. To the acetone solution was added 100 μL of *N*-trimethylsilyltrifluoroacetamide, and the resulting solution was analyzed by GLC (6 ft × 2 mm, 10% SE-30). The ratio of silylated *m*- and *o*-hydroxybenzoic acids was found to be 1:1.7 by comparison with authentic samples.

Acknowledgment. Financial support from the National Institutes of Health, Grant 1RO1-GM19103, is gratefully acknowledged.

Registry No.—**2**, 61812-51-9; **2** maleic anhydride adduct, 61812-48-4; **4**, 61812-52-0; **5**, 61812-53-1; maleic anhydride, 108-31-6.

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A Convenient Method for the α-Carbethoxylation of Alkylnitriles

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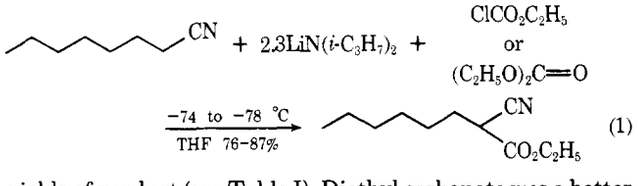
While carbethoxyl groups have been introduced in a number of instances into the α positions of acetonitriles substituted by phenyl groups,[2-4] only few examples are recorded when the acetonitriles are substituted by alkyl groups. With sodium ethoxide in diethyl carbonate[4] the yields are moderate and several hours heating at the boiling point and distillation of the ethanol produced are required to drive the reactions to products. Significant amounts of starting material are still recovered. For example, with this procedure capronitrile gives ethyl α-cyanocaproate in 54% yield along with starting material in 31% yield. An alternate procedure used by Hauser and Levine[5] to carbethoxylate acetonitrile with diethyl carbonate and sodium amide in refluxing ether gave ethyl cyanoacetate in only 40% yield and failed when extended to octanonitrile, octanamide forming instead in 30% yield after hydrolysis of the amidine intermediate.

Because alkylacetonitriles were recently monoalkylated[6] and benzeneselenylated[7] by way of the alkylacetonitrile anions formed using hindered dialkylamide bases, I attempted to carbethoxylate them analogously with diethyl carbonate or ethyl chloroformate. Using octanonitrile to optimize the conditions, it was found that 2.3 molar equiv of lithium diisopropylamide in tetrahydrofuran (THF) at −74 to −78 °C followed by 1.02–1.05 molar equiv of carbethoxylating agent gave high yields of ethyl hexylcyanoacetate (76–87%) after distillation (eq 1). Sodium hexamethyldisilamide gave lower



(1)

yields of product (see Table I). Diethyl carbonate was a better reagent to use than ethyl chloroformate, as the latter produced small amounts of ethyl *N,N*-diisopropylcarbamate as a side