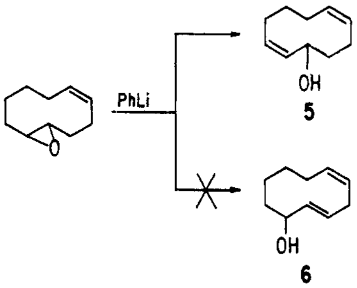
Scheme III



6 (Scheme III) were notably absent in all NMR spectra. Equilibration studies[21] and other considerations[22] indicate a strong conformational preference for the formation of **5**. However, ketonic products, whose presence would indicate rearrangement, were notably absent.[20]

These results complement other work with similar compounds[6,11] and help demonstrate the generality of the highly selective reaction pathways possible with unsaturated medium-ring epoxides.

Experimental Section

Reaction of Diethylmagnesium with *trans*-5,6-Epoxy-*cis*-cyclodecene. A solution of 1.52 g (10 mmol) of **1** in 20 mL of ether was added dropwise to 15 mL of an ice-cooled 0.6 M solution of diethylmagnesium.[23] After the solution was refluxed for 15 h, standard workup gave a mixture of **3** and **4** in an 85–90% yield. A sample of **3** was isolated by fractional distillation [bp 91–93 °C (20 mm); $n^{25}{}_{D}$ 1.4885; NMR (CCl_4) δ 4.3 (multiplet, 2 H) and 1.0–2.1 (multiplet, 14 H); M^+ (calcd) 152.1200 for $C_{10}H_{16}O$, found 152.1188]. Compound **4** was crystallized out of the residue at low temperature from ether/pentane. Its melting point was 40–42 °C; IR and NMR spectra were identical with those of an authentic sample.[12]

Preparation of *cis,cis*-2,7-Cyclodecadienol. Under argon atmosphere, approximately 20 mmol of phenyllithium[24] was freshly prepared in 30 mL of ether. A solution containing 2.28 g (15 mmol) of **1** in 10 mL of ether was added dropwise to the phenyllithium. After 8–12 h reflux, normal workup gave an oil which crystallized after 2 days in the freezer. The crude solid (2.28 g) was recrystallized from 50–70 °C-boiling petroleum ether yielding 1.62 g (72%) of **5** [mp 89.8–90.7 °C; IR (CCl_4) 3200–3650 (OH) and 708 cm^{-1} (cis CH=CH); NMR (CCl_4) δ 5.0–5.6 (m, 4, -CH=CH-), 4.15–4.60 (m, 1, CHO), and 1.1–2.5 (m, 11 remaining H); mass spectrum (75 eV) *m/e* 152 M^+ (10), 55 (94), and 29 (100)].

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.68; H, 10.72.

Acknowledgments. We wish to thank J. R. Olechowski for a generous sample of *cis,trans*-1,5-cyclodecadiene. P. S. Wharton kindly provided us with NMR and IR spectra of *syn*- and *anti*-$\Delta^{4(10)}$-octalol (**3**).

Registry No.—**1**, 24639-32-5; **3**, 41727-79-1; **4**, 61967-02-0; **5**, 61967-03-1; diethylmagnesium, 557-18-6; phenyllithium, 591-51-5.

References and Notes

(1) (a) Part 3 in the series "The Reactions of Organometallic Reagents with Unsaturated Epoxides". See C. B. Rose and S. K. Taylor, *J. Org. Chem.*, **39**, 578 (1974), for part 2. (b) NDEA Title IV Predoctoral Fellow, 1969–1972; abstracted in part from the doctoral dissertation of S. K. T.
(2) R. J. Anderson, *J. Am. Chem. Soc.*, **92**, 4978 (1970).
(3) R. W. Herr and C. R. Johnson, *J. Am. Chem. Soc.*, **92**, 4979 (1970).
(4) J. Staroscik and B. Rickborn, *J. Am. Chem. Soc.*, **93**, 3046 (1971).
(5) C. R. Johnson, R. W. Herr, and D. M. Wieland, *J. Org. Chem.*, **38**, 4263 (1973).
(6) E. D. Brown, J. K. Sutherland, and T. W. Sam, *J. Chem. Soc., Perkin Trans. 1*, 2332 (1975).
(7) J. Sicher, *Prog. Stereochem.*, **3**, 202 (1962).
(8) A. C. Cope, M. M. Martin, and M. A. McKervey, *Q. Rev., Chem. Soc.*, **20**, 119 (1966).
(9) J. A. Marshall, *Synthesis*, 517 (1972).
(10) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).
(11) W. Dittman and F. Stürzenhofecker, *Justus Liebigs Ann. Chem.*, **688**, 57 (1965).
(12) P. S. Wharton and D. W. Johnson, *J. Org. Chem.* **38**, 4117 (1973).
(13) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).
(14) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. K. Simeone, *J. Am. Chem. Soc.*, **92**, 2800 (1970).
(15) A. J. Birch and M. Smith, *Proc. Chem. Soc., London*, 356 (1962).
(16) G. H. Posner, *Org. React.*, **19**, (1972).
(17) A small vinyl peak at δ 5.5 in the NMR spectrum of **3** was essentially identical with that of the hydrocarbon analogue of $\Delta^{3(4)}$-octalol prepared by dehydration of *cis*-decahydronaphthol.
(18) E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 1218 (1960).
(19) We prepared **2** by the reaction shown in Scheme I and dehydrated it after the method described in ref 18. This method gave the exo isomer of **4** in low yield [NMR (CCl_4) δ 4.0 (m, CHOCH) and 1.0–2.0 (m, 14 H)]. The exo isomer had a narrower CHOCH multiplet than endoxodecalin (the latter compound has exo hydrogens which couple more strongly than the endo hydrogens of the former compound).
(20) See J. K. Crandall and L. C. Lin, *J. Org. Chem.*, **33**, 2375 (1968), and references cited therein.
(21) A. J. Hubert and J. Dale, *J. Chem. Soc. C*, 188 (1968).
(22) B. W. Roberts, J. J. Vollmer, and K. L. Servis, *J. Am. Chem. Soc*, **96**, 4578 (1974).
(23) F. H. Norton and H. B. Hass, *J. Am. Chem. Soc.*, **58**, 2147 (1936).
(24) L. A. Walter, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 757.

Stereospecific Thallium(III) Nitrate Mediated Conversion of Bicyclo[3.2.1]-2-octanone to *exo*-2-Norbornanecarboxylic Acid Methyl Ester[1a,b]

Anthony J. Irwin[1c] and J. Bryan Jones*

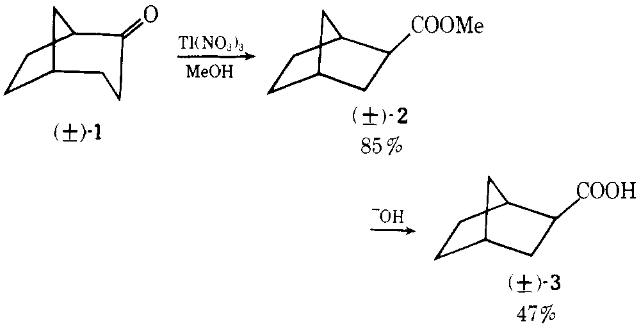
Department of Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 1A1

Received November 9, 1976

During absolute configuration assignments of bridged bicyclic products of some enzymic oxidoreduction reactions,[2] we carried out thallium(III) nitrate in methanol mediated homologation of (1*S*,4*R*)-2-methylenenorbornane to (1*S*,5*S*)-bicyclo[3.2.1]-2-octanone (**1**), a reaction similar to that first reported in the racemic series by Fărcaşiu and coworkers.[3] A methyl ester impurity was also formed in varying amounts during the reaction. This methyl ester, whose proportion we now find can reach as high as 31% under the homologation conditions, has been identified as *exo*-2-norbornanecarboxylic acid methyl ester (**2**).

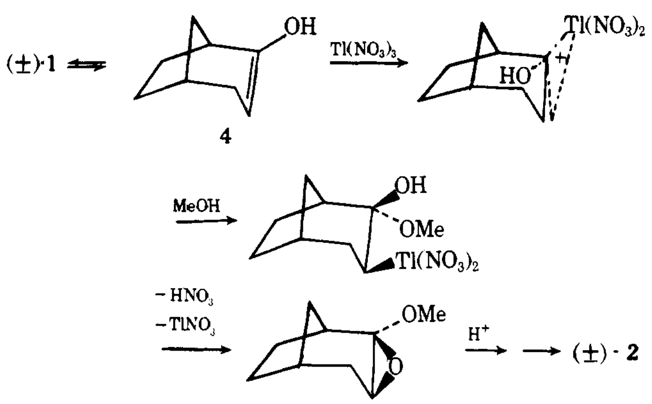
In view of the examples now available of ring contraction on treatment of six-membered cyclic ring ketones with thallium nitrate,[4–7] it seemed evident that **2** was formed from the initial homologation product **1**. This was confirmed by subjecting **1** itself to the thallium nitrate in methanol conditions. As shown in Scheme I, an 85% yield of **2**, characterized as the acid **3**, was obtained.

Scheme I



As in the steroid series,[6] the ring contraction is highly stereospecific, with none of the endo isomer of **2** being detected.[8] The exclusive formation of the exo ester **2** is consistent with the mechanism proposed by McKillop and Taylor,[5] with attack of the enol intermediate **4** by Tl^{3+} occurring from the exo direction as expected for electrophilic additions of this type.[9] The pathway envisaged is depicted in Scheme II.

Scheme II



Experimental Section[10]

Thallium(III) Nitrate Treatment of (±)-2-Methylenenorbornane. Thallium(III) nitrate[11] (2.67 g, 6 mmol) in methanol (20 mL) was added to (±)-2-methylenenorbornane [650 mg, 6 mmol, prepared as described for the (+) enantiomer[2]] in methanol (25 mL) at −10 °C. After being stirred for 30 min, the mixture was filtered and concentrated, and ether (50 mL) and 2 M hydrochloric acid (50 mL) were added. The mixture was shaken well and separated, and the aqueous phase was extracted three more times with ether. Evaporation of the dried ($MgSO_4$) ether extracts gave an oily product which contained (by GC analysis) 68% of 1 and 31% of 2. This mixture was treated directly with 15% ethanolic potassium hydroxide (30 mL) and warmed for 15 min on a steam bath. The mixture was then concentrated, diluted with water (100 mL), and washed four times with ether. The aqueous phase was acidified with concentrated hydrochloric acid and extracted four times with chloroform. The dried ($MgSO_4$) chloroform solution was evaporated to give a solid which after two sublimations gave *exo*-2-norbornanecarboxylic acid [(±)−3, 78 mg] as colorless crystals: mp 56–57 °C (lit.[12] mp 56–57 °C); IR 3330–2560 and 1725 cm^{-1}; NMR δ 1.0–2.0 (m, 8 H), 2.2–2.4 (m, 2 H), 2.5 (m, 1 H), and 11.2 ppm (br s, 1 H). No trace of *endo*-2-norbornanecarboxylic acid, NMR δ 1.1–1.8 (m, 8 H), 2.1–3.0 (overlapping m, 3 H), and 11.1 ppm (s, 1 H), could be detected.

Thallium(III) Nitrate Mediated Ring Contraction of Bicyclo[3.2.1]-2-octanone [(±)−1]. A solution of thallium(III) nitrate[11] (3.69 g, 8.3 mmol) in methanol (20 mL) was added to a stirred solution of the bicyclic ketone (±)−1 (1.03 g, 8.3 mmol) in methanol (30 mL) at 20 °C. After being stirred overnight the solution was filtered, concentrated, then diluted with water (50 mL), acidified with concentrated hydrochloric acid (2 mL), and finally extracted four times with ether. The combined ether phases were washed twice with brine, dried ($MgSO_4$), and then evaporated and distilled to give a colorless liquid [763 mg,bp 92–96 °C (12 Torr)] which contained (by GC analysis) unreacted ketone (±)−1 (15%) and the exo methyl ester (±)−2 (85%). This mixture was hydrolyzed with ethanolic potassium hydroxide and worked up as described above. The solid so obtained was sublimed twice to give colorless crystals of *exo*-2-norbornanecarboxylic acid [(±)−3, 544 mg, 48% yield], mp 55.0–56.5 °C, with spectral properties identical with those cited above.

Registry No.—(±)−1, 61242-42-0; (±)−2, 61967-04-2; (±)−3, 61967-05-3; thallium(III) nitrate, 13746-98-0; (±)-2-methylenenorbornane, 62014-79-3.

References and Notes

(1) (a) This work was supported by the National Research Council of Canada; (b) Abstracted from the Ph.D. Thesis of A. J. Irwin, University of Toronto, 1975; (c) Ontario Graduate Fellow, 1972–1973; National Research Council of Canada Scholar, 1973–1975.
(2) A. J. Irwin and J. B. Jones, *J. Am. Chem. Soc.*, **98**, 8476 (1976).
(3) D. Fărcaşiu, P. v. R. Schleyer, and D. B. Ledlie, *J. Org. Chem.*, **38**, 3455 (1973).
(4) K. B. Wiberg and W. Koch, *Tetrahedron Lett.*, 1779 (1966).
(5) (a) A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Org. Chem.*, **37**, 3381 (1972); (b) E. C. Taylor, C-S Chiang, A. McKillop, and J. F. White, *J. Am. Chem. Soc.*, **98**, 6750 (1976).
(6) (a) A. Romeo and G. Ortar, *Tetrahedron*, **28**, 5337 (1972); (b) G. Ortar and A. Romeo, *J. Chem. Soc., Perkin Trans. 1*, 111 (1976).
(7) J. Salaun, B. Garnier, and J. M. Conia, *Tetrahedron*, **30**, 1423 (1974).
(8) A control experiment showed that no epimerization of *endo*-2 or 3 would have occurred during the hydrolysis step.
(9) Cf. R. R. Sauers, H. M. How, and H. Feilich, *Tetrahedron*, **21**, 983 (1965).
(10) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. NMR spectra (Me_4Si internal standard) were obtained on a Varian T-60 instrument, IR data on chloroform solutions with a Perkin-Elmer 141 spectrometer, and GC analyses at 125 °C on an F & M 400 chromatograph equipped with 3 mm × 1 m columns of 2% QF-1 on Chromosorb G.
(11) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Lett.*, 5275 (1970).
(12) K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958).

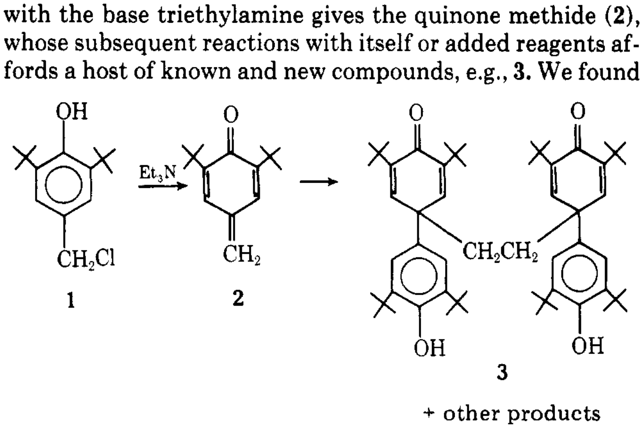
2,6-Di-*tert*-butyl-4,4-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,5-cyclohexadienone. A New Reaction Product of a Hindered Phenol

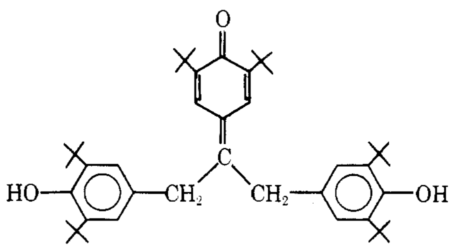
Dwight W. Chasar* and J. C. Westfahl

B. F. Goodrich Research and Development Center, Brecksville, Ohio 44141

Received October 13, 1976

The fate of hindered phenols in their performance as antioxidants continues to attract the attention of chemists.[1,2] Neureiter[3] and Starnes and co-workers[4] have shown that the reaction of 3,5-di-*tert*-butyl-4-hydroxybenzyl chloride (1) with the base triethylamine gives the quinone methide (2), whose subsequent reactions with itself or added reagents affords a host of known and new compounds, e.g., 3. We found that the reaction of the anion of dimethyl sulfoxide with 1 affords, along with other products, a heretofore unreported white, crystalline compound, mp 152–154 °C dec. The infrared spectrum (KBr) possesses absorptions at 3618 cm^{-1} (hindered phenol)[5] and at 1640 and 1655 cm^{-1} (conjugated carbonyl).[5] The ^1H NMR spectrum in deuteriochloroform has absorptions at 1.10 (9 H), 1.38 (18 H), 2.90 (2 H), 5.01 (1 H, exchangeable), 6.56 (1 H), and 6.81 ppm (2 H) downfield from internal Me_4Si.[6] All the absorptions were singlets. Structures 4 and 5 are consistent with these data.





4

The proton decoupled ^{13}C NMR spectrum, run under conditions[7] where errors in peak areas due to differing relaxation times (T_1) for the different carbons were eliminated, but assuming the nuclear Overhauser enhancement of all the carbons to be equal, showed that the actual structure contains one less carbon than 4. The ^{13}C NMR chemical shift data[8] are shown on the structure of 5. Structure 5 is also supported by its UV spectrum, which in methanol possesses absorptions at