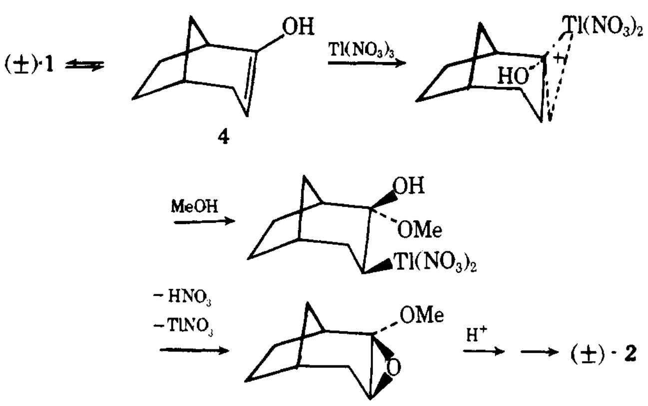
Scheme II



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.
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(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).
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(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.
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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

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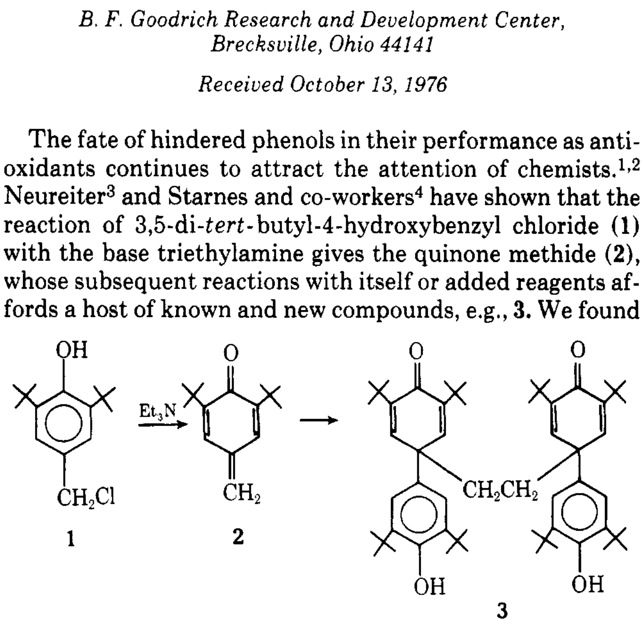
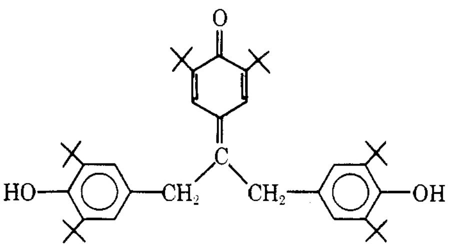
Received October 13, 1976

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.

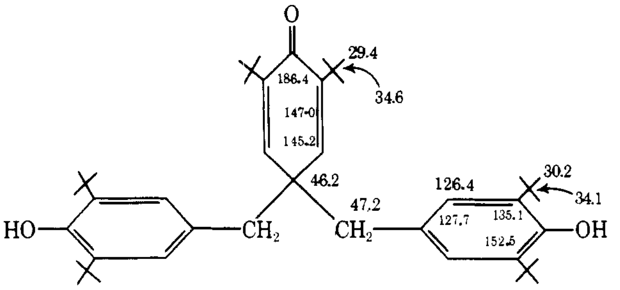


+ other products



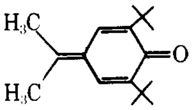
4

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



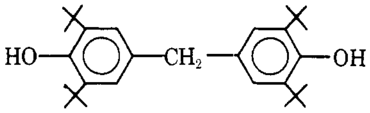
5

231 (ϵ 23 000) and 272 nm (5200). This compares favorably with that of **3**, which has absorptions at 235 (ϵ 37 000), 277 (4500), and 365 nm[3] (47). This is in contrast to **6**, the analogy to **4**, which has λ_{max} at 317 nm (ϵ 30 000).



6

The mass spectrum of **5** did not reveal an M^+ peak but did give intense fragments at *m/e* 424 and 219, consistent with **7** and **8**, respectively. Indeed, a chloroform solution of **5** standing at room temperature for a day or two or refluxed for a few hours rapidly developed a yellow color. TLC of this solution indicated two primary products along with **5**. The major product was isolated in pure form by preparative TLC and was shown to compare exactly with authentic **7** by TLC, melting point, and IR. The second component, always contaminated by **5**, was orange. Its NMR[4a] and color were consistent with **9**. These components (**7** and **9**) also accompanied the formation of **5** in the initial synthesis, as determined by TLC.



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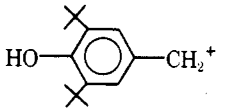

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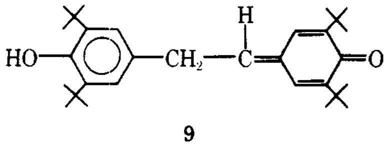
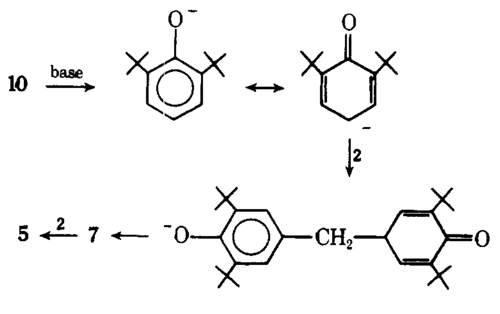


9

The mechanism of formation of **5** from **1** and dimsyl anion requires that a one-carbon extrusion take place. Since this did not seem too likely,[9] we felt that we may be isolating a product which results from a reaction of **2** with an impurity, namely, 2,6-di-*tert*-butylphenol (**10**), which is present, as determined by TLC, in the 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol used to make **1**. A similar conclusion was drawn by Neureiter[3] in his isolation of **3**. Thus, the following mechanism[10] could account for the formation of **5**.



Further credence was lent to this proposed mechanism by carrying out the following experiments. When **1**, which was TLC free of **10** (by using pure 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol to form **1**), was reacted with the dimsyl anion, no **5** was observed. However, when pure **1** was converted to **2** using triethylamine[3] in benzene instead of the dimsyl anion and subsequently reacted with **7** (or **10**), **5** was produced in yields comparable to those from the Me_2SO reactions. Thus, the nature of the base is unimportant, while **7** appears to be a probable intermediate in the formation of **5**.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and are uncorrected. All TLC analyses were performed on Analtech, Inc., precoated glass plates of silica gel using 7:3 hexane–benzene as the eluent and UV and visible light and iodine vapor for visualization. The preparative scale plates were 1000-μm thick silica gel on glass from Analtech. The elemental analysis was obtained on a CHN analyzer at the Avon Lake Technical Center of B. F. Goodrich Co. The ^{1}H NMR spectra were obtained on a Varian Model A-60 and the ^{13}C NMR spectrum on a Bruker Model HX-90E. The mass spectrum was obtained on a Perkin-Elmer Model 270.

3,5-Di-*tert*-butyl-4-hydroxybenzyl Chloride (1). Concentrated HCl (300 mL, 3.6 mol) was added to a slurry of unpurified 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol (236 g, 1.0 mol, Ethyl Corp.) in hexane and was stirred at ambient temperature overnight under nitrogen. The resulting two layers were separated and the hexane layer washed with water, dried ($MgSO_4$), and evaporated to afford 245.5 g (96.5%) of a yellow-orange liquid,[3] whose IR and NMR were consistent with the desired structure. When purified (recrystallization from hexane and then benzene) benzyl alcohol was used, **1** was pale yellow.

2,6-Di-*tert*-butyl-4,4-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)2,5-cyclohexadienone (5). Sodium amide (1.0 g, 0.026 mol) was added to dry Me_2SO (15 mL) at 25 °C under nitrogen. The mixture was heated to 50 °C and kept there for 2 h. Upon cooling to 25 °C, **1** (6.52 g, 0.026 mol, prepared from unpurified benzyl alcohol) in Me_2SO (15 mL) was added dropwise over 2 h. The temperature rose to 30 °C. The resulting blue-green mixture was poured into acidic water to give a yellow precipitate, which was removed by vacuum filtration and dried in a vacuum desiccator. This solid (6.16 g) was slurred in boiling methanol (40–50 mL), cooled, filtered, and washed to afford a faintly yellow solid. This material was boiled in methanol (400 mL) and filtered hot to remove an insoluble white solid,[11] mp 286–287 °C. The mother liquor was concentrated to crystallize 0.8 g of **5**, mp 152–154 °C, which was shown to be TLC pure. A second crop can also be taken. Anal. Calcd for $C_{44}H_{66}O_3$: C, 82.17; H, 10.37. Found: C, 82.90; H, 10.62.

Acknowledgment. We would like to thank Tim Pratt and Charles Jacobs for assisting with some of the reactions, R. Whitehead for the UV work, K. Welch for the mass spectral work, and F. Baron for the analytical data. Discussions with Professor Paul D. Bartlett and comments by referees were also very valuable.

Registry No.—**1**, 955-01-1; **5**, 62078-82-4; 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol, 88-26-6.

References and Notes

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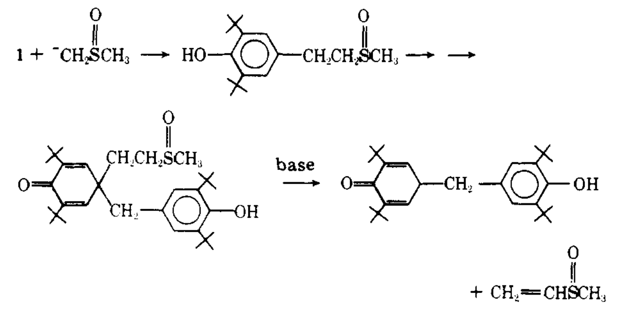
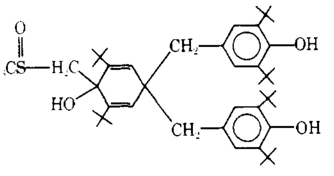
(5) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy", Academic Press, New York, N.Y., 1963.
(6) By comparison, **3** in deuteriochloroform possessed chemical shifts of 1.31 for the quinoid *tert*-butyl, 1.40 for the aromatic *tert*-butyl, 5.1 for the hindered phenolic hydroxyl, 6.43 for the quinoid ring hydrogens, and 6.97 for the aromatic ring hydrogens (downfield from internal Me_4Si).[3]
(7) The FFT spectrum was obtained on a 16% solution in deuteriochloroform by making 54 scans using a 300-s interval between scans, with a pulse width of 11.5 μs (90°) and a 6000 Hz sweep width.
(8) The assignments of chemical shifts to the various carbon atoms were made based upon the peak heights and are downfield from the ^{13}C signal of Me_4Si.
(9) A mechanism can be devised wherein a one-carbon extrusion could be accomplished by the intimate participation of the dimsyl anion in the mechanism, e.g.



Attempts to trap methyl vinyl sulfoxide using anthracene, a Michael receptor, failed.

(10) We thank referee 1 for his fruitful comments and suggestions concerning the mechanism.

(11) This compound could not be unequivocally identified. Owing to its very low solubility, a satisfactory NMR spectrum could not be obtained, although it appeared to possess two different *tert*-butyl groups and a methyl group. The infrared spectrum (KBr) showed absorptions at 3618 and 3400 cm^{-1}, indicating both hindered and bound hydroxyl groups; a single peak at 1638 cm^{-1}, unlike the doublet characteristic of cyclohexadienones,[3] suggesting a nonconjugated double bond; and an absorption at 1020 cm^{-1} possibly due to a sulfoxide absorption. The mass spectrum gave an apparent parent ion at *m/e* 728 ± 4. A spray reagent used to detect sulfoxides on TLC plates[12] gave a positive test. Based upon these data, a possible structure would be an adduct between the dimsyl anion and **5**, e.g.



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A Dramatic Solvent Effect in the Diels–Alder Reactions of Ortho Benzoquinones

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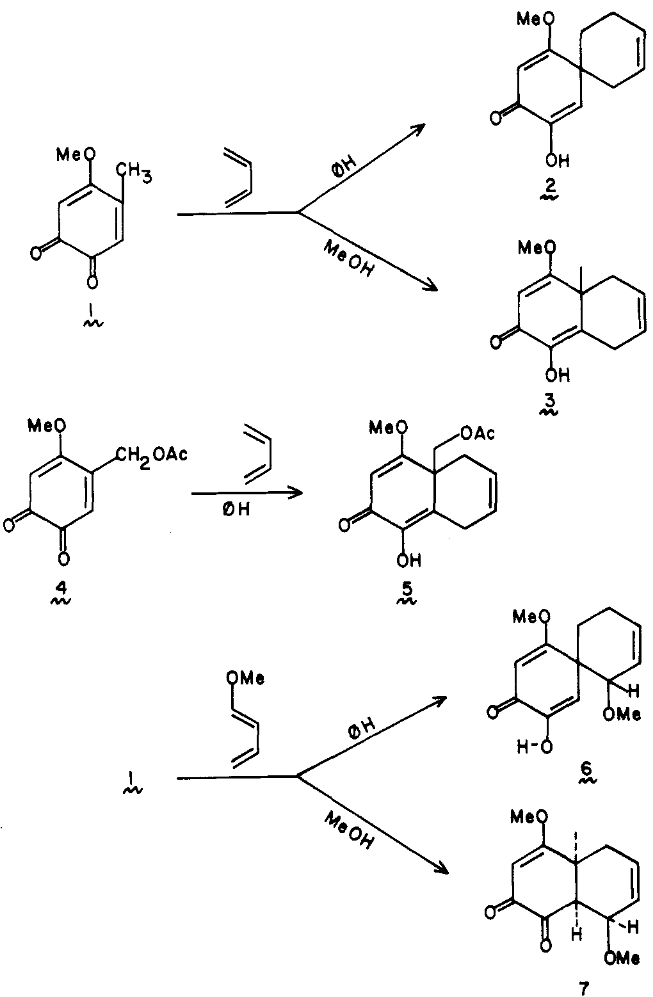
Conventional wisdom has it that solvent effects are of relatively nominal importance in determining the course of Diels–Alder reactions.[1] This might be expected in the light of the concerted nature perceived for the [2 + 4] cycloaddition process.[2]

Recently we have investigated the efficacy of 5-substituted 4-methoxy-1,2-benzoquinones as dienophiles.[3,4] Compound **1** *reacts with 1,3-butadiene in benzene quite slowly.* Upon heating at 105 °C (sealed tube) for 5 h, a 60% yield of "abnormal" adduct **2** was obtained.[3] Under these conditions we did not isolate any of the expected "normal" product **3**, though the absence of an authentic sample precluded a definitive statement as to whether small amounts of **3** might have been produced. Curiously, this "abnormal" process, involving enolization of the 5-alkyl group followed by cycloaddition to the tautomeric quinone methide,[5] is quite structure dependent since, under the same conditions, ortho quinone **4** gives only the expected product **5**.[4] In studying Diels–Alder reactions of compound **4**, we found that cycloaddition occurred more rapidly and efficiently when the reactions were conducted in methanol. Accordingly, it was of interest to examine the cycloaddition of **1** with 1,3-butadiene in this solvent.

Reaction of **1** with 1,3-butadiene in methanol at 100 °C (sealed tube) for 20 h gave, upon rapid chromatography on Florisil, a 63% yield of a crystalline 1:1 adduct, mp 103.5–104 °C, whose spectral properties clearly define it to be the "expected" product, **3**.[6] Examination of the NMR spectrum of the crude reaction mixture indicated the presence of ca. 12% of abnormal adduct **2**.[7] Thus a pronounced solvent effect is observed in promoting the course of the two modes of Diels–Alder reaction of **1** with 1,3-butadiene.[8]



A similar trend was observed in studying the cycloaddition of **1** with *trans*-1-methoxybutadiene. In benzene, upon heating under reflux for 6 h, a 37% yield of spiro adduct **6**, mp 110–111 °C, is obtained.[9] Since the compound is rather unstable to chromatography, a clearer definition of the competing processes was provided by examination of the NMR spectrum of the crude reaction mixture. This indicated a 5:1 ratio of **6**:**7** (vide infra). Conversely, when the reaction was conducted in methanol under reflux, a 67% yield of normal adduct **7**, mp 118.5–119.5 °C, was obtained after chromatography on Florisil. NMR analysis prior to chromatography indicated the ratio of **6**:**7** to be ca. 1:10.[7]

We have studied the effect of mixed solvents on the course of these cycloadditions. Using a 1:1 molar mixture of methanol–benzene (100 °C, sealed tube) reaction of **1** with butadiene gave essentially the same product distribution (**7** ≫ **6**) as with pure methanol. However, reaction of **1** with 1-methoxybutadiene in 1:1 molar methanol–benzene gave ca. a 1:1 mixture of **7**:**6**.

Clearly, these data do not allow for a precise definition of the role of solvents in determining the course of Diels–Alder products. However, they suggest that solvent manipulation may be of more useful consequence in producing desired results than has been hitherto supposed.

Experimental Section[10]

Diels–Alder Reaction of Quinone (1) with 1,3-Butadiene in Absolute Methanol. Formation of *dl*-1-Hydroxy-4-methoxy-