(+)-morphine (**10**) showed interesting central effects when injected intracerebrally in rats, suggesting the existence of multiple morphine receptors in the brain.[14]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Elemental analyses were performed by the Section on Microanalytical Services and Instrumentation of this Laboratory. The identity and chemical purity of **3–11** were confirmed by direct comparison with authentic samples of the enantiomeric (−) series. IR, NMR (using tetramethylsilane at δ 0.0 as an internal reference), and mass spectra were obtained on Perkin-Elmer 257, Varian Model HR-220, and Hitachi RMU-6E (70 eV) instruments, respectively. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter. Silica gel GF plates for analytical and preparative TLC were purchased from Analtech, Inc., Newark, Del.

7(*R*)- and 7(*S*)-(+)-Dihydrosinomenine (2a and 2b). Sinomenine (**1**; 16.6 g, 50.40 mmol) was dissolved in MeOH (450 mL) and hydrogenated using 10% Pd/C as a catalyst until the absorption of hydrogen stopped at approximately 1 mol. After filtration of the catalyst, the solvent was evaporated to give an oil residue which solidified on the addition of ether (200 mL), and the product was collected by filtration. This product (16.5 g) melted at 190–195 °C (lit.[7] mp 198 °C) and was used for conversion to **3** without further purification. Preparative TLC of a portion (150 mg) of this mixture of position 7 epimers over silica gel GF (Et_2O–MeOH, 9:1) gave as the major component the lower R_f 7*R* epimer (100 mg, 67%), which showed, after crystallization from $CHCl_3$–Et_2O (1:10), mp 196.5–197.5 °C; $[\alpha]^{23}_D$ +121° (*c* 1.28, $CHCl_3$); IR ($CHCl_3$) 1733 cm^{-1}; NMR ($CDCl_3$) δ 6.60 (2 H, AB system, J = 8 Hz, aromatic H), 6.44 (1 H, brd s, OH), 4.30 (1 H, d, J = 13 Hz, C-5 equatorial H), 3.90 (1 H, dd, J = 7, 12 Hz, C-7 axial H), 3.80 (3 H, s, aromatic OCH_3), 3.43 (3 H, s, C-7 OCH_3), 2.41 (3 H, s, N–CH_3), 2.25 (1 H, d, J = 13 Hz, C-5 axial H).

Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; N, 4.23. Found: C, 69.04; H, 7.54; N, 4.18.

The higher R_f 7*S* epimer (39 mg, 26%) was obtained as the minor isomer and showed, after crystallization from $CHCl_3$–Et_2O (1:10), mp 196.5–197.5 °C; $[\alpha]^{23}_D$ +87° (*c* 1.49, $CHCl_3$); IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 6.64 (2 H, dd, J = 8 Hz, aromatic H), 6.26 (1 H, brd s, OH), 4.07 (1 H, d, J = 13 Hz, C-5 equatorial H), 3.82 (3 H, s, aromatic OCH_3), 3.36 (1 H, t, J = 3.5 Hz, C-7 equatorial H), 3.30 (3 H, s, C-7 OCH_3), 2.73 (1 H, d, J = 13 Hz, C-5 axial H), 2.42 (3 H, s, N–CH_3).

Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; N, 4.23. Found: C, 69.08; H, 7.54; N, 4.13.

(+)-Dihydrocodeinone (3). The mixture of **2a** and **2b** from above (3.00 g, 9.05 mmol) and polyphosphoric acid (Matheson, Coleman and Bell, 60 g) was heated at 65–70 °C for 1.25 h while stirring. The cooled reaction mixture was basified by the careful addition of ammonium hydroxide (28%) at 0 °C, saturated with NaCl, and extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and evaporated to afford a solid, which was recrystallized from Et_2O–$CHCl_3$ (3:1) to give **3** (1.98 g, 73%): mp 196 5–197.5 °C (lit.[9] mp 197–198 °C); $[\alpha]^{23}_D$ +205.3° (*c* 0.9, $CHCl_3$) [lit.[3] $[\alpha]_D$ +207.4° ($CHCl_3$)].

Conversion of (+)-Dihydrocodeinone (3) to (+)-Codeine (9). (+)-Codeine (**9**) was prepared from (+)-dihydrocodeinone (**3**) essentially as described by Rapoport[6] in the (−) series via the following intermediates. (+)-Dihydrocodeinone dimethyl ketal **4**: mp 121–122 °C; $[\alpha]^{23}_D$ +167.2° (*c* 1.1, EtOH) [lit.[15] (−) enantiomer of **4**: mp 122–123 °C, $[\alpha]_D$ −151° (*c* 0.9, EtOH)]. (+)-8,14-Dihydrothebaine (**5**): mp 162–165 °C; $[\alpha]^{23}_D$ +268.6° (*c* 1.1, C_6H_6) [lit.[4c] mp 162–163 °C, $[\alpha]_D$ +268.2° (*c* 1.544, C_6H_6)]. (+)-7-Bromodihydrocodeinone dimethyl ketal **6**: mp 116–117 °C; $[\alpha]^{23}_D$ +165.1° (*c* 1, $CHCl_3$) [lit.[4c] mp 117 °C, $[\alpha]_D$ +164.5° (c 1.536, $CHCl_3$)]. Treatment of **6** with potassium *tert*-butoxide at 25 °C (48 h) instead of 60 °C[6] gave (+)-codeinone dimethyl ketal **7**: mp 135–136.5 °C; $[\alpha]^{23}_D$ +238.3° (*c* 1.2, EtOH) [lit.[4c] mp 138 °C, $[\alpha]_D$ +236° (*c* 1.016, EtOH)]. Hydrolysis of **7** with 5% HCl (0.5 h, 75 °C) instead of AcOH–H_2O[6] gave (+)-codeinone (**8**): mp 185–186 °C; $[\alpha]^{23}_D$ +204.5° (*c* 1, EtOH) [lit.[4d] mp 186 °C, $[\alpha]_D$ +206.0° (EtOH)]. Reduction of **8** with $NaBH_4$ in MeOH gave (+)-codeine (**9**): mp 157.5–158.5 °C; $[\alpha]^{23}_D$ +136.2° (*c* 0.7, EtOH) [lit.[4a] mp 158 °C, $[\alpha]^{25}_D$ +137.4° (*c* 0.743, EtOH)].

(+)-Morphine (10). To a stirred solution of BBr_3 (6.00 g, 24 mmol) in $CHCl_3$ (70 mL) was added **9** (1.167 g, 3.9 mmol) in $CHCl_3$ (10 mL) at 23–26 °C over a 2-min period, and stirring was continued for 15 min. The reaction mixture was poured into a stirred mixture of ice (32 g) and NH_4OH (28% NH_3, 8 mL) and stirred for 30 min at 0 °C. The crystalline material which formed was filtered, washed with cold $CHCl_3$ and then water, and dried to give **10** (800 mg). The aqueous phase from the filtrate was saturated with NaCl and extracted with $CHCl_3$–EtOH (3:1). The combined extracts were evaporated, and the residue was purified by silica gel thin-layer chromatography using $CHCl_3$–MeOH (8:2) as a solvent to yield **10** (241 mg). Total yield was 88%. Recrystallization from MeOH gave **10**·H_2O as colorless prisms: mp 253–255 °C; $[\alpha]^{23}_D$ +132.1° (*c* 0.49, MeOH) [lit.[4a] mp 247–248 °C, $[\alpha]^{23}_D$ +132.1° (*c* 0.383, MeOH)].

Anal. Calcd for $C_{17}H_{19}NO_3$·H_2O: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.47; H, 7.25; N, 4.63.

(+)-Heroin (**11**). A mixture of **10** (285 mg, 1 mmol) and acetic anhydride (2 mL) was heated at 90–100 °C for 4 h. Ether was added to the cooled solution, and the mixture was basified with 10% KOH while cooling. The ether phase was separated, the aqueous phase was extracted with ether, and the combined extracts were dried over Na_2SO_4. The solvent was evaporated to give a solid, which was recrystallized from AcOEt to afford **11** (295 mg, 80%): mp 169–170.5 °C; $[\alpha]^{23}_D$ +176° (*c* 0.63, MeOH) [lit.[13] (−) enantiomer of **11**: mp 173 °C, $[\alpha]^{25}_D$ −166.4° (*c* 1.49, MeOH)].

Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.28; H, 6.28; N, 3.79. Found: C, 67.97; H, 6.37; N, 3.44.

Acknowledgment. We would like to thank Drs. Mario Aceto, Louis Harris, and Everette L. May, Medical College of Virginia, for their encouragment. The analgesic screening of the compounds mentioned was carried out by Mrs. Louise Atwell of our laboratory. We also thank Dr. Mikio Takeda, Tanabe Seiyaku Research Laboratory, and Dr. Wataru Nagata, Shionogi Seiyaku Research Laboratory, for the generous gifts of (−)-sinomenine used in this work.

Registry No.—**1**, 115-53-7; **2a**, 65120-75-4; **2b**, 65120-76-5; **3**, 64520-24-7; **4**, 65165-95-9; **5**, 65165-96-0; **6**, 65165-97-1; **7**, 65165-98-2; **8**, 65494-91-9; **9**, 64520-25-8; **10**, 65165-99-3; **11**, 65166-00-9.

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Cleavage of Tetrahydrofuran by Lithium Bis(2,6-di-*tert*-butylphenoxy)aluminum Hydride

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Received August 16, 1977

The reaction of lithium aluminum hydride ($LiAlH_4$) with 2 or 3 molar equiv of 2,6-di-*tert*-butylphenol (I) at room temperature gives lithium bis(2,6-di-*tert*-butylphenoxy)-aluminum hydride (II; eq 1). This is confirmed in Table I for

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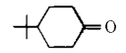
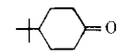
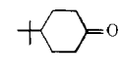
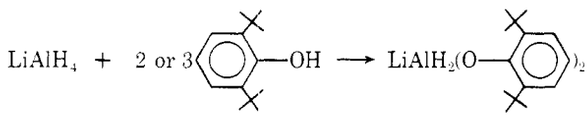
Table I. Reaction of Lithium Aluminum Hydride with Phenols in THF

Entry	$LiAlH_4$, mol	Phenol	Amount, mol	Reflux time, h	Ketone	Amount, mol	% redn	H_2 evol[a]
1	0.010	I	0.020	16				0
2	0.015	PhOH	0.030	19				0.029
3	0.020	I	0.060	16		0.01	0[b]	0
4	0.015	I	0.045	5		0.011	0[c]	0
5	0.015	I	0.045	0		0.01	96[d]	0.013

[a] Moles of H_2 evolved on hydrolysis. [b] Recovered 97% ketone; GLC analysis using 3,3,5,5-tetramethylcyclohexanone as an internal standard. [c] Recovered 93% ketone; GLC analysis using the same internal standard; traces of alcohols present. [d] Alcohol ratio was 53% cis and 47% trans (normalized to 100%).

reactions in tetrahydrofuran (THF), and in each case 2 molar equiv of H_2 are evolved as measured by a wet test meter. A



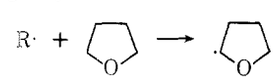
I II

$$+ 2H_2 \quad (1)$$

third 2,6-di-*tert*-butylphenoxy group is difficult to introduce presumably due to steric hindrance.[1,2] On refluxing the clear colorless solutions very little additional H_2 is evolved in the experiments using 3 molar equiv of I,[3] and in all the experiments with I no hydrogen is evolved on hydrolysis with 10% sulfuric acid after the reflux period (Table I, entries 1, 3, and 4). Refluxing of the hydride solutions was carried out under a blanket of nitrogen, although oxygen was not rigorously removed from the system. The absence of hydrogen on hydrolysis implies that no Al–H bonds are present after refluxing, and this was confirmed by the virtual absence of reduction of 4-*tert*-butylcyclohexanone added after the reflux period (Table I, entries 3 and 4). The recovered ketone is unreacted rather than formed by hydrolysis of an enolate as shown by (1) a carbonyl stretching band at 1706 cm^{-1} in the IR spectrum of a reaction mixture sampled prior to hydrolysis, (2) the absence of gas evolution during addition of the ketone, and (3) in an experiment in which $LiAlH_4$ was added to a reaction mixture prior to hydrolysis, the epimeric alcohol ratio was found to be 86% trans and 14% cis, close to that reported for the reduction of 4-*tert*-butylcyclohexanone with $LiAlH_4$ in THF.[4]

On the other hand, in the absence of heating the hydride species II reduces 4-*tert*-butylcyclohexanone in a normal manner, giving 53% cis and 47% trans alcohols with very little residual ketone (Table I, entry 5).

A solution formed by the reaction of $LiAlH_4$ (0.04 mol) with I (0.08 mol) in THF and refluxed for 18.5 h was hydrolyzed with water and sodium hydroxide solution[5] (no H_2 evolution occurred on hydrolysis), and the product was distilled. *n*-Butyl alcohol (0.061 mol) was isolated and identified by IR, NMR, and GLC comparison with an authentic sample. This alcohol undoubtedly was formed from the cleavage of THF by II on heating. The cleavage of THF can be explained by two different mechanisms. One involves radical formation (eq 2) followed by ring opening of the tetrahydrofuranyl radical.[6] Radical cleavage of the THF ring could result in the formation of an aldehyde[7] group which would be reduced by II, thus

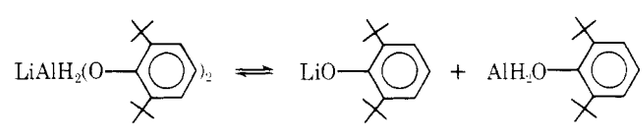


(2)

accounting for the destruction of the Al–H bonds. Assuming that no free I remains after the reaction of 2 molar equiv of I with $LiAlH_4$, the radicals must initially be produced by thermal homolysis of Al–O–C_6H_3-2,6-(t-Bu)$_2$ bonds. Thermal homolysis of an Al–C bond has been observed with diphenyltritylaluminum.[8] In this case a stable triphenylmethyl radical was formed, while in the present example a relatively stable phenoxyl radical would be produced.

A direct attack of the hydride species II on THF via a polar mechanism seems unlikely, although it cannot be ruled out, from a consideration of the markedly different behavior of phenol itself, as shown in Table I, entry 2. After refluxing a THF solution of lithium aluminum diphenoxyhydride (III) for 19 h, acidic hydrolysis produced the calculated quantity of residual hydrogen, and the original number of hydride equivalents in $LiAlH_4$ was quantitatively accounted for. If the sterically hindered reagent II was able to directly attack THF, the less hindered and electronically similar reagent III would be expected to do the same.

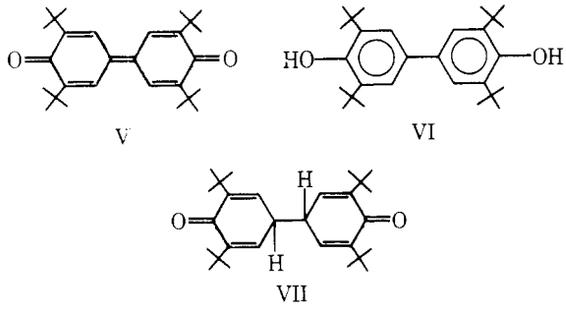
It is conceivable that II exists in equilibrium with a tricoordinate aluminum species IV, as shown by eq 3.[9] Species



II IV (3)

IV can form a complex with THF, leading to its reduction. If this mechanism is correct, then the formation of IV may be attributed to steric hindrance inherent in species II (as compared with its absence in III).

There is another difference in behavior between phenol and I. With the reagent III the reaction mixture remained clear and colorless before and after heating. In the reactions of I a deep yellow to orange color always developed soon after the reflux period. Small amounts of a dark brown crystalline solid were isolated. Various samples of this material melted fairly sharply between 206 and 209 °C. The solid was shown to be an approximately equimolar mixture of 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (V) and the diphenol VI by NMR, IR, and UV comparison with samples of V and VI prepared independently. Compounds V and VI are probably formed from the phenol I by radical reactions, possibly involving compound VIII as an intermediate.[10] 2,6-Di-*tert*-butylphenoxy radicals can combine through the para positions to form VI.[11] The isolated dark brown crystalline mixture of V and VI is much darker in color than each of the separate components. This may be due to quinhydrone-type complex formation in the solid state. Evaporation of a THF solution of V and VI gave a similar deep brown solid. A quinhydrone complex of the

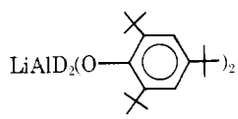


V VI

VII

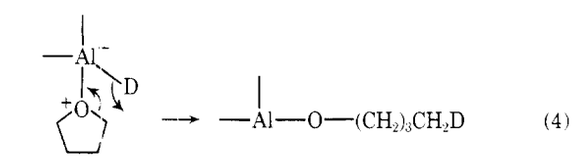
methyl analogues of V and VI (*tert*-butyl groups replaced by methyl) has been reported.[12]

In order to distinguish between the radical mechanism of ring cleavage and a polar mechanism involving a tricoordinate aluminum reagent such as IV, the deuterated reagent VIII was

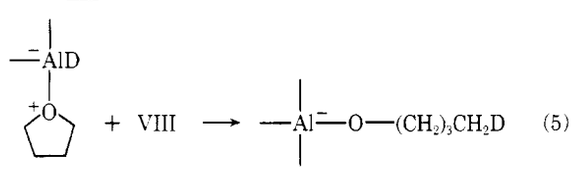


VIII

prepared by the reaction of $LiAlD_4$ with 2,4,6-tri-*tert*-butylphenol[14] in THF. The reaction mixture was refluxed, and following hydrolysis with aqueous base,[5] the deuterated *n*-butyl alcohol was isolated by distillation. Analysis by NMR spectroscopy clearly showed the product to be $CH_2DCH_2CH_2CH_2OH$. Thus, the radical mechanism involving the formation and reduction of an aldehyde is ruled out, and a mechanism involving cleavage by a tricoordinate aluminum species such as IV is supported. The mechanism can either involve intramolecular (eq 4) or intermolecular (eq 5) attack by hydride.



(4)



(5)

The radical reactions leading to products V and VI are apparently unrelated to the cleavage of THF.

Experimental Section

2,6-Di-*tert*-butylphenol (I) was obtained from the Aldrich Chemical Co. and was fractionally distilled through a 12-in helix-packed column, giving a clear colorless distillate, bp 105 °C (8 mm). 2,4,6-Tri-*tert*-butylphenol was purified by recrystallization from aqueous ethanol. Lithium aluminum deuteride was obtained from the Alfa Ventron Corp. 4-*tert*-Butylcyclohexanone was purified by distillation. Tetrahydrofuran was distilled from $LiAlH_4$ through a helix-packed column immediately before use. $LiAlH_4$ solutions in THF were obtained from the Alfa Ventron Corp., and the molarity was checked by measurement of hydrogen evolution on reaction with a phenol–THF solution. GLC analysis was carried out with a Hewlett Packard Model 5750 instrument. NMR analysis was carried out on a Jeol MH-100 instrument.

Preparation of Lithium Bis(2,6-di-*tert*-butylphenoxy)aluminum Hydride (II). A 100-mL three-neck flask with a magnetic stirring bar was flamed under nitrogen, and 10 mL of a 1.0 M $LiAlH_4$–THF solution was added by pipet in a drybox. The flask was then fitted under nitrogen with a reflux condenser and an equilibrated dropping funnel and attached to a wet test meter separated from the flask by a $CaSO_4$ trap. The nitrogen was discontinued, and a solution of the phenol (I; 4.12 g, 0.02 mol) in THF was added dropwise with stirring. After the addition the reaction flask was disconnected from the wet test meter and again placed under a nitrogen atmosphere and heated under reflux (oil bath) for 16 h. On cooling under nitrogen the reaction mixture turned deep yellow. Hydrolysis of the reaction mixture attached to the wet test meter with 10% H_2SO_4 resulted in no gas evolution.

In experiments involving the addition of 4-*tert*-butylcyclohexanone, the reaction mixture was worked up by extracting with ether, washing the organic layer consecutively with saturated $NaHCO_3$ and NaCl solutions, and drying over anhydrous $MgSO_4$. The solutions were concentrated by distillation through a helix-packed column and analyzed by GLC on an 12 ft × ⅛ in 5% Carbowax 20M column at 136 °C after addition of an internal standard.

Preparation of 3,3′,5,5′-Tetra-*tert*-butyldiphenoquinone (V). 2,6-Di-*tert*-butylphenol (I) was oxidized by alkaline ferricyanide according to the procedure of Cook, English, and Wilson.[13] The product consisted of reddish brown needles: mp 245–247 °C (lit. mp 240–241,[12] 246 °C[8]); IR (carbonyl band) 1600 cm^{-1} (s); NMR ($CDCl_3$) δ 1.38 (s, 36 H), 7.66 (s, 4 H).

Preparation of 4,4′-Dihydroxy-3,3′,5,5′-tetra-*tert*-butyldiphenol (VI). The diphenoquinone V (1g, 0.0025 mol) in 20 mL of THF was reduced with 0.01 mol of $LiAlH_4$. Hydrolysis with water and 10% H_2SO_4 gave yellow needles after recrystallization from 95% ethanol: mp 185–187 °C (lit.[8] mp 185 °C); IR (OH stretch) 3610 cm^{-1} (s, sharp); NMR (CCl_4) δ 1.47 (s, *tert*-butyl), 4.92 (s, OH), 7.06 (s, ring H's).

Acknowledgment. The support (to H.H.) of the Faculty Research Award Program, The City University of New York, Grants 11419 and 10198, is gratefully acknowledged.

Registry No.—I, 128-39-2; II, 54004-00-1; V, 2455-14-3; VI, 128-38-1; $LiAlH_4$, 16853-85-3; phenol, 108-95-2; 4-*tert*-butylcyclohexanone, 98-53-3; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; tetrahydrofuran, 109-99-9.

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