Novel Rearrangement and Cyclization Processes Resulting from Bromination of 1,1-Dibenzyltetralin Derivatives

Bernard Miller* and Xiaolian Shi†

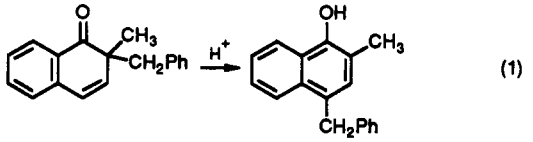
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received September 27, 1991

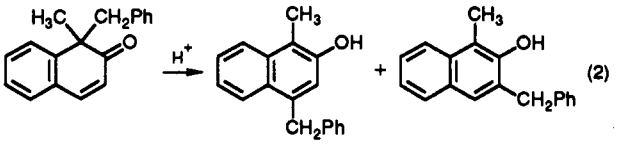
Addition of bromine to hydrocarbon **1** results in an aromatic alkylation to form the bicyclo[3.3.1]nonane derivative **5**. Addition of bromine to ketone **3** in acetonitrile solution results in a dienone–phenol rearrangement to form phenol **6**, while reaction of ketone **4** with phosphorus pentabromide yields phenols **10** and **11**. This reaction results from a novel "bromo ketone–phenol" rearrangement, as demonstrated by the fact that bromo ketones **12** and **13** spontaneously isomerize to **10** and **11**.

Reactions of naphthalenone derivatives with electrophilic reagents have often been observed to yield surprising products. Although 4,4-dialkyl-1-naphthalenone derivatives undergo simple dienone–phenol rearrangements in acid,[1] 1,1-dialkyl-2-naphthalenones and 2,2-dialkyl-1-naphthalenones yield products of "abnormal" dienone–phenol rearrangements, resulting from migration of the oxygen functions as well as of the alkyl groups.[2]

Our group has reported that migrations of allyl groups in 1-allyl-2-naphthalenones may result in formation of products of [1,2], [1,4], [1,5], or [3,4] migrations, depending on the nature of substituents on the allyl groups and on the solvent (acetic acid or acetic anhydride) employed.[3] Migrations of benzyl groups were found to proceed by [1,3] paths in rearrangement of a 2-benzyl-1-naphthalenone (eq 1) and by [1,4] and [1,5] paths in rearrangement of a 1-benzyl-2-naphthalenone (eq 2).[3]



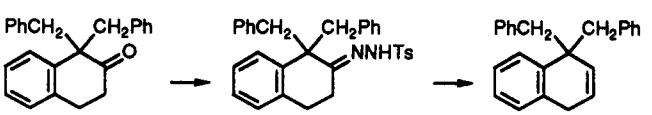
(1)



(2)

Recently, as part of a program aimed at preparing novel "isoaromatic" molecules, we have studied reactions of halogenating agents with 1,1-dibenzyltetralin derivatives. These studies have yielded a new crop of unusual reactions, including a bromine-initiated dienone–phenol rearrangement,[4a] a "bromo ketone–phenol" rearrangement,[4b] and a bromine-initiated Friedel–Crafts reaction.[4a] These reactions are described in this paper.

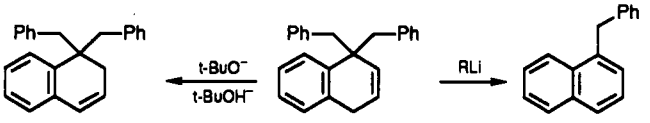
Synthesis of 1,1-Dibenzyltetralin Derivatives. 1,1-Dibenzyl-1,4-dihydronaphthalene (**1**) was prepared by reaction of the tosylhydrazone of 1,1-dibenzyl-2-tetralone with *n*-butyllithium or methyllithium in ether or tetrahydrofuran solutions. Use of excess lithium reagents or,



1

to a minor extent, prolonged reaction times or reaction in tetrahydrofuran rather than ether solutions resulted in lowered yields. These conditions tended to result in formation of 1-benzylnaphthalene at the expense of formation of **1**.

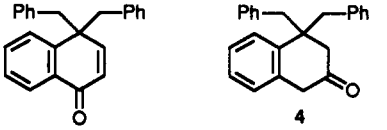
Formation of 1-benzylnaphthalene was shown to result from a secondary reaction of lithium reagents with the initially formed hydrocarbon **1**, presumably by elimination of a benzyl anion from the intermediate allylic anion formed by abstraction of a diallylic proton from **1**. Aromatization of **1** is quite a rapid reaction. Reaction of **1** with a 0.3 M solution of *n*-butyllithium in 2:1 THF–hexane for 15 min at room temperature results in complete conversion of **1** to 1-benzylnaphthalene. Despite the ease of the elimination, however, formation of 1-benzylnaphthalene from **1** does not appear to be a concerted process, since prolonged refluxing of **1** with potassium *tert*-butoxide in *tert*-butyl alcohol yields the allylic rearrangement product **2** rather than 1-benzylnaphthalene. Thus, in a protic solvent, protonation of the intermediate anion can compete successfully with loss of a benzyl anion.



2 1

Elimination of hydrocarbon anions from a 1,4-dihydrobenzene derivative on reaction with organosodium derivative at 145 °C has been reported.[5] However, we are not aware of any other reported instance of fragmentation of a hydrocarbon on reaction with an organolithium reagent or under such mild conditions as those required for fragmentation of **1**.

Oxidation of **1** by chromyl chloride yielded 4,4-dibenzyl-1-naphthalenone (**3**), and reaction of **1** with disiamylborane, followed by chromic acid oxidation of the resulting alcohol, yielded 4,4-dibenzyl-2-tetralone (**4**).



3 4

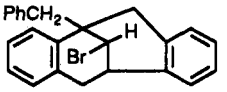
Reaction of 1 with Bromine. Addition of 1 equiv of bromine to a solution of **1** in carbon tetrachloride resulted in almost instantaneous decolorization of the solution but simultaneously generated hydrogen bromide vapors. Evaporation of the solvent gave a quantitative yield of a

† Permanent address: Department of Chemistry, Zhejiang University, Hangzhou, PRC.

(1) E.g.: Arnold, R. T.; Buckely, J. S., Jr.; Richter, J. *J. Am. Chem. Soc.* **1947**, *69*, 2322.
(2) Marvell, E. N.; Geiszler, A. O. *J. Am. Chem. Soc.* **1952**, *74*, 1259. Marvell, E. N.; Magoon, E. *J. Am. Chem. Soc.* **1954**, *76*, 5118.
(3) Miller, B.; Saidi, M. R. *J. Am. Chem. Soc.* **1976**, *98*, 2227.
(4) Preliminary accounts of these reactions have been reported: (a) Shi, X.; Day, R.; Miller, B. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1166. (b) Miller, B.; Shi, X. *Tetrahedron Lett.* **1988**, *29*, 5099.
(5) Pines, H.; Eschinazi, H. E. *J. Am. Chem. Soc.* **1956**, *78*, 5950.

0022-3263/92/1957-1677$03.00/0

single compound, $C_{24}H_{21}Br$, mp 164–165 °C. X-ray crystallographic analysis established its structure as the bicyclo[3.3.1]nonane derivative **5**.

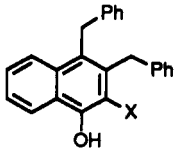


5

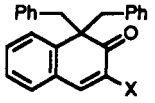
Examination of the NMR spectrum of the reaction mixture during the course of the reaction, or immediately after completion of the addition of bromine, gave no indication of the presence of products other than **5**, which thus appears to be the initial product of the reaction.

Reaction of 3 with Bromine. In contrast to the rapid reaction of **1** with bromine in carbon tetrachloride, no reaction could be observed between bromine and ketone **3** under the same conditions, even after prolonged reaction times. Similarly, **3** did not react with bromine in acetonitrile solution at 0 °C, but reaction did occur, requiring ca. 20 min for complete decolorization of the bromine, in acetonitrile solution at room temperature. Hydrogen bromide was again evolved during the reaction. No cyclization product corresponding to **5** was obtained. The only product isolated was a brominated phenol, **6**.

To establish the identity of **6**, ketone **3** was subjected to a dienone–phenol rearrangement in acetic acid–sulfuric acid solution. The resulting phenol was, as expected, 3,4-dibenzyl-1-naphthol (**7**). This structural assignment was supported by the fact that its melting point was much higher than the reported melting point[6] of the only other reasonable product, 2,4-dibenzyl-1-naphthol, and that its ^1H NMR spectrum showed a singlet at δ 6.70, characteristic of protons ortho to the hydroxy groups of 1-naphthols. Reaction of **7** with bromine in acetic acid yielded phenol **6**, identical with that obtained from reaction of **4** with bromine.



6, X = Br
7, X = H



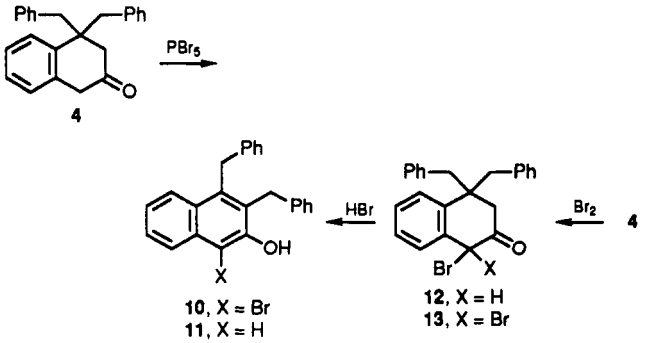
8, X = H
9, X = Br

To check the possibility that formation of **6** actually resulted from a rearrangement process initiated by hydrogen bromide rather than bromine, a sample of **3** was dissolved in acetonitrile saturated with hydrogen bromide. No reaction was observed even after 18 h. Thus, formation of **6** from **3** proceeded via a rearrangement induced by bromine rather than acid.

In contrast to the rearrangement of **3**, ketone **8** reacted normally with bromine, yielding an addition product which formed ketone **9** on elimination of hydrogen bromide.

Reaction of Bromine and Phosphorus Pentabromide with 4. In an attempt to convert the carbonyl group to a vinyl bromide, ketone **4** was reacted with a large excess of phosphorus pentabromide in benzene. Rather than the desired bromide, the only product isolated was a phenol, **10**, isomeric with **6**. When the reaction was repeated employing just 1 mol of phosphorus pentabromide, a more complex phenolic mixture was obtained. Its ^1H NMR spectrum showed the presence of diaryl methylene singlets at δ 4.29 and 4.43, corresponding to peaks appearing in the spectrum of **10**, but showed additional singlets at δ 4.21 and 4.41. The product mixture could not readily be separated, so phenol **10** was debrominated by reduction with zinc in acetic acid. The resulting phenol, **11**, had NMR peaks at δ 4.21 and 4.41 and had TLC R_f values, employing a variety of solvent systems, identical with those of the prinicpal product obtained from reaction of **4** with 1 mol of phosphorus pentabromide.

The only phenols which could reasonably be obtained from **4** are those resulting from [1,2] or [1,4] migrations of benzyl groups. The possibility of [1,4] migrations could readily be eliminated, since the NMR spectra of both phenols showed one benzyl group to be in a β-position, and since phenol **11** showed no signal for a proton in an β-position ortho to the hydroxy group. Furthermore, the spectrum of **10** showed a signal for an aromatic proton at a far downfield position (δ 8.11), suggesting a proton peri to the *bromine* atom. Thus, the structures of **10** and **11** must be 1-bromo-3,4-dibenzyl-2-naphthol and 3,4-dibenzyl-2-naphthol, respectively.



10, X = Br
11, X = H

12, X = H
13, X = Br

To check the hypothesis that phosphorus pentabromide acted as a brominating agent during conversion of **4** to **10** and **11**,[7] ketone **4** was reacted with bromine in carbon tetrachloride at −10 °C. Reaction with 2 mol of bromine, followed quickly by washing with sodium bicarbonate to remove hydrogen bromide, yielded the expected dibromide (**12**) as a pale yellow oil whose structure was clearly demonstrated by its spectra (see the Experimental Section). Ketone **12** was stable for seveal days at room temperature, or several weeks at 0 °C. However, attempts to purify it by chromatography, or simply allowing it to remain at room temperature for prolonged periods, invariably resulted in its rearranging to phenol **10**. If the hydrogen bromide produced by the bromination were not rapidly neutralized, **12** rearranged completely to **10** in 2–3 h at room temperature.

Reaction of **4** with 1 mol of bromine yielded a mixture containing unreacted **4**, **12**, and (principally) the monobromo ketone **13**, identified by an ^1H NMR signal at δ 4.72. On standing, this mixture rearranged to a mixture whose ^1H NMR spectrum resembled that obtained from reaction of **4** with 1 mol of phosphorus pentabromide.

Discussion

Conversion of **1** to **5** by reaction with bromine appears to be an unique instance of the occurrence of a Friedel–Crafts reaction in the course of addition of bromine to a double bond. Benzene and toluene are common solvents for addition of bromine to olefins, and no Friedel–Crafts reactions have been reported to accompany addition. Even compounds capable of intramolecular formation of five- or six-membered rings (e.g., derivatives of 4-phenyl-1-

(6) Setkina, V. N.; Kursanow, D. N. *Izv. Akaad. Nauk. SSSR, Otdel Khim. Nauk, 1951, 81*; *Chem. Abstr.* **1952**, *46*, 459a.

(7) Phosphorus pentabromide can react as an electrophilic brominating agent at high temperatures. (Mikhailov, B. M.; Promyslov, M. S. *Zhur. Obshchei. Khim.* **1950**, *20*, 338), but we are not aware of other examples of such reactions with ketones.

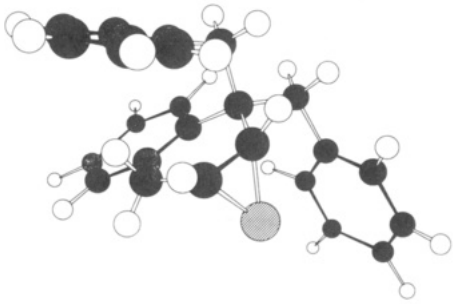


Figure 1. Molecular mechanics generated model of the bromonium ion from **1**, generated using parameters for a thiarane ring in place of the bromonium ring.

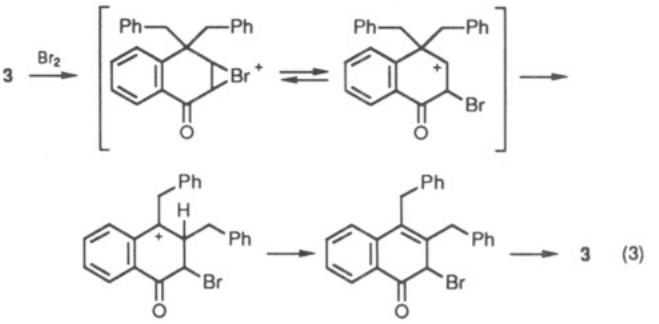
butene and 5-phenyl-1-pentene) have uniformly been reported to add bromine without intervention of ring substitution processes.

Examination of molecular models or of figures generated by a molecular mechanics program[8] show that the most stable conformation of hydrocarbon **1** has one of the phenyl groups lying over the dihydroaromatic ring. In this conformation an ortho position of the "eclipsed" phenyl ring closely approaches C-3 of hydrocarbon **1**. The bromonium ion resulting from reaction of **1** with bromine (Figure 1) would be ideally positioned for a Friedel–Crafts cyclization.

The "eclipsed" relationship of the two rings has other, perhaps equally significant effects. The normal attack of a bromide ion at the rear of the bromonium ion would be strongly inhibited by the presence of the eclipsing phenyl group, as would abstraction of a hydrogen ion from C-4 to yield an allylic bromide. Thus, the normally uncompetitive attack of a bromonium ion on an aromatic ring might compete successfully with formation of a dibromide or allylic halide.

However, Wagner–Meerwein migrations of alkyl groups occur frequently during additions of halogen to double bonds,[9] and there seems to be no compelling reason why such a rearrangement should not occur in the bromonium ion from **1**. It is true that benzyl groups, although excellent migrators in reactions such as the dienone–phenol rearrangement,[10] in which the migrating group can be assumed to have appreciable cationic character, have frequently been found to be poor migrators in Wagner–Meerwein rearrangements.[11] Nonetheless, we remain quite surprised that a Friedel–Crafts attack by a bromonium ion on a monoalkyl-substituted benzene ring should be more rapid than a Wagner–Meerwein shift to form a tertiary benzylic cation.

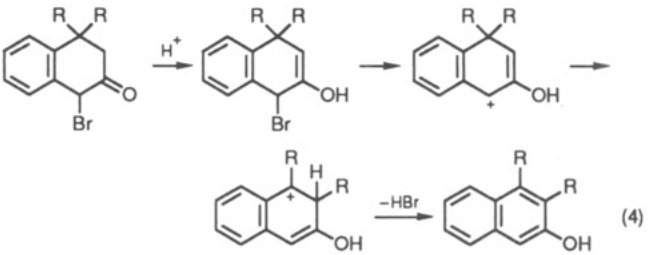
Rearrangement does occur, to the exclusion of any Friedel–Crafts cyclization (or of any bromine addition, presumably due to the steric effects described above), in reaction of naphthalenone **3** with bromine. Although the overall result of that reaction is a dienone–phenol rearrangement, the mechanism of the bromine-initiated rearrangement (eq 3) is undoubtedly quite different from



those of other dienone–phenol rearrangements. While the electrophiles in other dienone–phenol rearrangements attack the carbonyl groups, the bromine molecule must attack the carbon–carbon bond of **3**. Thus, while the transition states in other dienone–phenol rearrangements appear to resemble carbocations complexes to aromatic rings, the transition state for the rearrangement step in the bromine-initiated reaction of **3** should more closely resemble a typical Wagner–Meerwein rearrangement.

As was mentioned above, benzyl groups are not necessarily good migrators in Wagner–Meerwein rearrangements. However, a Friedel–Crafts cyclization to form a bicyclo[3.3.1]nonane system would presumably require the development of an appreciable positive charge at the carbon α to the carbonyl group. We assume that this effect is sufficient to inhibit cyclization and allow the migration of a benzyl group to occur instead.

Finally, the evidence presented above suggests that the rearrangements of ketone **4** and of bromo ketones **12** and **13** proceed by the mechanism shown in eq 4.



Formation of allylic cations from **12** and **13** has ample precedent, since migrations of bromine atoms in α-bromo ketones appear to proceed via such cations.[12] However, we are not aware of the occurrence of other skeletal rearrangements in the course of halogen migration. In **12** and **13** the rearrangements may be facilitated by the fact that the cyclohexadienyl rings in the transition states may attain an appreciable degree of aromatic character. In this respect "bromo ketone–phenol" rearrangements closely resemble dienone–phenol rearrangements. Benzyl groups, as has been mentioned above, are excellent migrators in dienone–phenol rearrangements, and we believe the bromo ketone–phenol rearrangements are greatly facilitated by the fact that the migrators are benzyl groups rather than simple alkyl groups.

Experimental Section

Melting points are corrected. ^{1}H NMR spectra were taken in deuteriochloroform solution unless otherwise noted. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

1,1-Dibenzyl-3,4-dihydro-2(1*H*)-naphthalenone. A solution of 2-tetralone (10.0 g, 0.064 mol) in 50 mL of *tert*-butyl alcohol was added in portions to a solution of potassium *tert*-butoxide

(8) These figures were generated using force field geometry optimizations from the program MODEL for Digital Equipment Corporation VAX VMS operating system. This was made available by Professor K. Stelion of the University of Montréal.

(9) E.g.: Roberts, J. D.; Trumbull, E. R., Jr.; Bennett, W.; Armstrong, R. *J. Am. Chem. Soc.* **1950**, *72*, 3116. Kwart, H.; Kaplan, L. *J. Am. Chem. Soc.* **1953**, *75*, 3356; **1954**, *76*, 4078; Meinwald, J.; Wiley, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 3667. Norman, R. O. C.; Thomas, C. B. *J. Chem. Soc. B* **1967**, 598. Wilt, J. W.; Gutman, G.; Ranus, W. J.; Zigman, A. R. *J. Org. Chem.* **1967**, *32*, 893. Cristol, S. J.; Nachtigall, G. W. *J. Org. Chem.* **1967**, *32*, 3727.

(10) Miller, B. *J. Am. Chem. Soc.* **1970**, *92*, 6252.

(11) House, H. O.; Grubbs, E. J.; Gannon, W. F.; *J. Am. Chem. Soc.* **1960**, *82*, 4099. Warrick, P., Jr.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 4095. Owen, J. R.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 5809.

(12) Miller, B.; Wong, H.-S. *Tetrahedron* **1972**, *28*, 2369.

(14.5 g, 0.129 mol) in 150 mL of *tert*-butyl alcohol. The resulting deep blue solution was cooled in ice and shaken while a solution of benzyl chloride (16.1 g, 0.128 mol) in 50 mL of *tert*-butyl alcohol was added in portions over a 30-min period. The reaction mixture was allowed to stand, with frequent shaking, for an additional hour, and water (ca. 1 L) was added. The resulting mixture was twice extracted with methylene chloride, and the organic layer was washed twice with water and dried over magnesium sulfate. The solvent was evaporated, and the solid product was recrystallized from ethanol to give 1,1-dibenzyl-3,4-dihydro-2(1*H*)-naphthalenone (16.1 g, 0.049 mol, 77%) as white needles: mp 104–104.5 °C; ^{1}H NMR δ 1.83 (m, 4 H), 3.20 (d, J = 12.8 Hz, 2 H), 3.56 (d, J = 12.8 Hz, 2 H), ca. 6.5–7.5 (m, 13 H), 7.7 (dd, J = 7.2, 1.8, 1 H); IR (mineral oil) ν_{max} 1704, 1160, 1061, 780, 752, 743, 703 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O$: C, 88.30; H, 6.79. Found: C, 88.08; H, 6.93.

1,1-Dibenzyl-3,4-dihydro-2(1*H*)-naphthalenone *p*-Toluenesulfonylhydrazone. A solution of 1,1-dibenzyl-3,4-dihydro-2(1*H*)-naphthalenone (18.8 g, 0.058 mol), *p*-toluenesulfonylhydrazine (30.0 g, 0.162 mol), and 7.0 mL of concd. hydrochloric acid in 150 mL of methanol was heated under reflux for 36 h, resulting in the deposition of white crystals. The mixture was cooled in ice and filtered, and the resulting solid was recrystallized from ethanol to yield the hydrazone (25.9 g, 90.4%) as white crystals: mp 177–179 °C dec; ^{1}H NMR δ 1.53 (m, 4 H), 2.43 (s, 2 H), 3.24 (d, J = 12.1 Hz, 2 H), 3.35 (d, J = 12.1 Hz, 2 H), 6.3 (m, 4 H), ca. 6.8 (m, ca. 7 H), 7.1–7.9 (m, ca. 5 H), 8.12 (d, J = 7.1 Hz, 2 H); IR (mineral oil) ν_{max} 3142, 1579, 1147, 920, 699 cm^{-1}. Anal. Calcd for $C_{31}H_{30}N_2O_2S$: C, 75.43; H, 5.92; N, 5.67. Found: C, 75.51; H, 6.04; N, 5.59.

1,1-Dibenzyl-1,4-dihydronaphthalene (1). The tosylhydrazone of 1,1-dibenzyl-1,4-dihydro-2(1*H*)-naphthalenone (17.3 g, 0.031 mol) in 150 mL of anhydrous ether under nitrogen was stirred and cooled in ice, and a 1.40 M solution of methyllithium in ether (46 mL, 0.064 mol) was added over a 30-min period. Bubbling became vigorous after addition of half the methyllithium and continued for about 10 min after completion of the addition. The ice bath was then removed, and stirring was continued for an additional 20 min. Water was added, cautiously at first, and the layers were separated. The ether layer was washed with aqueous sodium chloride solution and dried over magnesium sulfate, and the solvent was evaporated to yield a deep yellow oil (9.4 g). The oil was chromatographed on neutral alumina, eluting with cyclohexane, to yield hydrocarbon 1 (8.20 g, 0.0267 mol, 85%) as a pale yellow oil: ^{1}H NMR δ 2.53 (bs, 2 H), 2.92 (d, J = 1.31 Hz, 2 H), 3.20 (d, J = 13.1 Hz, 2 H), 5.61 (m, 2 H), 6.95 (m, 13 H), 7.07 (dd, J = 7.3, 1.8 Hz, 1 H); IR (neat) ν_{max} 1599, 1490, 1449, 1029, 752, 733, 702 cm^{-1}. Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.84; H, 6.81.

Reaction of 1 with *n*-Butyllithium. A solution of 1.0 M *n*-butyllithium in hexane (10 mL, 0.01 mol) was added to a stirred solution of 1 (0.50 g, 0.0016 mol) in 20 mL of tetrahydrofuran at room temperature. The addition time was 15 min. Immediately after completion of the addition, the flask was cooled in ice and water was added. Ether was added, and the layers were separated. The organic layer was washed with water and dried over magnesium sulfate, and the solvent was evaporated to give a pale brown oil which crystallized on standing. Recrystallization from ethanol gave 0.31 g (0.0014 mol, 89%) of 1-benzylnaphthalene as white crystals: mp 57–58 °C (lit.[13] mp 57.5–58 °C); ^{1}H NMR δ 4.37 (s, 2 H), ca. 3.2 (m, 12 H).

1,1-Dibenzyl-1,2-dihydronaphthalene (2). A solution of hydrocarbon 1 (1.0 g, 0.032 mol) in 5 mL of *tert*-butyl alcohol was added to a solution of potassium *tert*-butoxide (0.80 g, 0.071 mol) in 30 mL of *tert*-butyl alcohol. The mixture was stirred and heated at reflux for 17 h. Water was then added, followed by sufficient ice to bring the solution to room temperature. Ether was added, and the layers were separated. The organic layer was washed twice with water, dried over magnesium sulfate, and the solvent evaporated to give a brown oil which was chromatographed on alumina. Elution with petroleum ether gave 1,1-dibenzyl-1,2-dihydronaphthalene (0.77 g, 0.0025 mol, 77%) as a pale yellow oil: ^{1}H NMR δ 2.19 (d, J = 4.5 Hz, 2 H), 2.97 (d, J = 12.7 Hz, 2 H), 3.01 (d, J = 12.7 Hz, 2 H), 5.77 (dt, J = 9.7, 4.5 Hz, 1 H), 6.37 (d, J = 9.7 Hz, 1 H), 7.08 (m, 14 H); IR ν_{max} 1594, 1489, 1449, 751, 699 cm^{-1}. Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 93.01; H, 7.05.

Reaction of Bromine with 1,1-Dibenzyl-1,4-dihydronaphthalene. A solution of hydrocarbon 1 (2.0 g, 6.5 mmol) in 20 mL of carbon tetrachloride was cooled to 0 °C in an ice–salt bath and stirred while a solution of bromine (1.1 g, 7.5 mmol) in 40 mL of carbon tetrachloride was added over a period of 10 min. Stirring was continued at 0 °C for an additional 0.5 h, and the solvent was then removed at room temperature on a rotary evaporator employing a mechanical pump. The resulting pale brown solid (2.5 g) was recrystallized from ethanol to give beautiful white crystals: mp 164–165 °C (1.8 g, 4.6 mmol, 71%); ^{1}H NMR (in C_6D_6 solution, 200 MHz) δ 2.64 (d, J = 9.6 Hz, 1 H), 2.73 (d, J = 10.6 Hz, 1 H), 3.2 (m, 2 H), 3.37 (d, J = 13.8 Hz, 1 H), 3.58 (d, J = 13.8 Hz, 1 H), 3.99 (dd, J = 16.7, 5.9 Hz, 1 H), 4.38 (d, J = 4.2 Hz, 1 H), 6.6–7.8 (m, 13 H). Anal. Calcd for $C_{24}H_{21}Br$: C, 74.01; H, 5.44; Br, 20.53. Found: C, 74.01; H, 5.33; Br, 20.70. Crystal data: $C_{24}H_{21}Br$, M = 389.34. Triclinic space group $P\bar{1}$ (No. 2), a = 9.566 (3) Å, b = 12.097 (4) Å, c = 18.341 (4) Å, α = 71.41 (2), β = 75.10 (2), γ = 66.97 (3), V = 1825.6 (9) Å^3, Z = 4, D_c = 1.413 g cm^{-3}, F(000) = 800, $\mu_{MoK\alpha}$ = 22.3 cm^{-1}. The crystal used for the study (cut to dimensions of 0.33 × 0.33 × 0.50 mm) was mounted in a thin-walled glass capillary tube which was sealed as a precaution against moisture sensitivity. Preliminary examination and data collection were performed with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer at an ambient temperature of 23 ± 2 °C. A total of 4181 unique reflections were measured ($+h$, $\pm k$, $\pm l$; θ–2θ scan mode, $2\theta_{max}$ = 43°). An empirical absorption correction based on ψ scans was applied (0.767–1.00 on I).

The structure was solved by using Patterson difference Fourier techniques and was refined by full-matrix least-squares methods [function minimized: $W(|F_o| - |F_c|)^2$, $w^{1/2} = 2F_oL_p/\sigma_I$]. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions as fixed isotropic scatterers. The final agreement factors were R = 0.035 and R_w = 0.045 for the 2964 reflections having $I \geq 3\sigma_I$. All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

Tables of atomic coordinates and bond lengths and angles are available on request from the Director of the Cambridge Crystallographic Data Centre, University of Cambridge Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for ref 4a.

1,1-Dibenzyl-2(1*H*)-naphthalenone (8). A solution of *n*-butyllithium in hexane (7.5 mL, 1.6 M) was added slowly to a solution of diisopropylamine (1.2 g, 12 mmol) in 50 mL of anhydrous THF kept in a dry ice–acetone bath. The solution was stirred for 5 min, and a solution of 1,1-dibenzyl-3,4-dihydro-2-(1*H*)-naphthalenone in 15 mL of THF was added. After stirring for an additional 30 min, a solution of benzeneselenyl bromide (2.8 g, 12.0 mmol) in 20 mL of THF was added over a 10-min period. The dry ice bath was removed, and after 10 min a solution of 1 mL of acetic acid in 5 mL of water was added, followed by dropwise addition of 7 mL of 30% hydrogen peroxide. When the gas evolution had ended, water and ether were added and the two layers were separated. The organic layer was washed with dilute hydrochloric acid and then twice with water and dried over magnesium sulfate, and the solvent was evaporated to yield a yellow oil which crystallized on standing. Recrystallization from methanol yielded 2.9 g, (8.95 mmol, 84%) of 1,1-dibenzyl-2-(1*H*)-naphthalenone: mp 95–96 °C (lit.[14] mp 96–97 °C); ^{1}H NMR δ 3.25 (d, J = 13.9 Hz, 2 H), 3.67 (d, J = 13.9 Hz, 2 H), 5.82 (d, J = 7.8 Hz, 1 H), 6.7 (m, ca. 4 H), 6.8 (m, ca. 6 H), 7–7.5 (m, ca. 3 H), 7.61 (dd, J = 6.4, 1.6 Hz, 1 H).

3-Bromo-1,1-dibenzyl-2(1*H*)-naphthalenone (9). A solution of bromine (0.30 g, 1.9 mmol) in 2 mL of carbon tetrachloride was added to a solution of 1,1-dibenzyl-2(1*H*)-naphthalenone (8) (0.61 g, 1.9 mmol) in 5 mL of carbon tetrachloride at room temperature. The mixture was shaken briefly and allowed to stand at room temperature for 30 min. The solvent was then evaporated under

(13) Borsche, W.; Hofmann, P.; Kuhn, H. *Liebigs Ann.* **1943**, *554*, 22.

(14) Curtin, D. Y.; Tuites, R. C.; Dybrig, D. H. *J. Org. Chem.* **1960**, *25*, 155.

vacuum, and the product was recrystallized from ethanol to yield 9 (0.70 g, 77%) as white crystals: mp 148.5–149.5 °C; ^{1}H NMR δ 3.30 (d, J = 13.1 Hz, 2 H), 3.73 (d, J = 13.1 Hz, 2 H), 6.6–7.7 (m, 15 H); IR (KBr) 1669, 1493, 1455, 1352, 769, 753, 708(s), 614 cm^{-1}. Anal. Calcd for $C_{24}H_{19}BrO$: C, 71.47; H, 4.75; Br, 19.81. Found: C, 71.65; H, 4.75; Br, 19.94.

Synthesis of 4,4-Dibenzyl-1,4-dihydro-1-naphthalenone (3). A solution of *tert*-butyl chromate (9.7 g, 0.056 mol) in 120 mL of carbon tetrachloride was added slowly to a solution of hydrocarbon 1 (8.0 g, 0.026 mol) in 80 mL of carbon tetrachloride. The mixture was heated under reflux for 2 h, and the solvent was evaporated under vacuum on a rotary evaporator, heating with a steam bath. The residue was mixed with a saturated solution of sodium bisulfite and heated on a steam bath for 1 h. After it had cooled to room temperature, the mixture was extracted with methylene chloride, and the organic layer was twice extracted with sodium bisulfite solution and then with water and dried over magnesium sulfate. Evaporation of the solvent gave a pale brown solid which was recyrstallized from ethanol to give 3 as pale yellow crystals (4.0 g, 0.12 mol, 47%): mp 114.5–116 °C; ^{1}H NMR δ 3.27 (d, J = 13.3 Hz, 2 H), 3.42 (d, J = 13.3 Hz, 2 H), 6.27 (d, J = 10.1 Hz, 1 H), ca 6.6–7.1 (m, 11 H), 7.1–8.02 (m, 4 H); IR (KBr) ν_{max} 1660 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O$: C, 88.88; H, 6.22. Found: C, 88.79; H, 6.05.

Synthesis of 3,4-Dibenzyl-1-naphthol. Ketone 3 (0.22 g, 0.68 mmol) was dissolved in 2 mL of acetic acid, and 0.1 mL of concd sulfuric acid was added. The solution was shaken briefly and allowed to stand at room temperature for 15 h. Water was then added, and the mixture was extracted with methylene chloride. The methylene chloride solution was washed with water, with sodium bicarbonate solution, and again with water and was dried over magnesium sulfate. Evaporation of the solvent left a brown solid which was recrystallized from ethanol to give 3,4-dibenzyl-1-naphthol (0.14 g, 0.43 mmol, 68%) as white needles: mp 135.5–137 °C; ^{1}H NMR δ 4.02 (s, 2 H), 4.38 (s, 2 H), 6.70 (s, 1 H), 7.15 (m, ca. 14 H); IR (mineral oil) ν_{max} 3534, 1239, 1212, 1091, 1069, 855, 764, 746, 724, 709, 694 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O$: C, 88.88; H, 6.22. Found: C, 88.87; H, 6.34.

Reaction of 4,4-Dibenzyl-1,4-dihydro-1-naphthalenone with Bromine. A solution of bromine (0.60 g, 3.8 mmol) in 20 mL of acetonitrile was added in portions to a stirred solution of ketone 3 (1.0 g, 3.1 mmol) in 30 mL of acetonitrile at room temperature. The color had largely faded after ca. 10 min, and fumes of HBr were produced. Stirring was continued for an additional hour, after which the solvent was evaporated to yield a pale brown solid. This was recrystallized from methanol to give 2-bromo-3,4-dibenzyl-1-naphthol as a pale yellow solid (1.0 g, 2.5 mmol, 80%): mp 143–145 °C; ^{1}H NMR δ 4.43 (s, 2 H), 4.48 (s, 2 H), 6.20 (s, 1 H), 7.1–7.9 (m, 14 H); IR (mineral oil) ν_{max} 3415 cm^{-1}. Anal. Calcd for $C_{24}H_{19}BrO$: C, 71.47; H, 4.75; Br, 19.81. Found: C, 71.24; H, 4.80; Br, 20.10.

4,4-Dibenzyl-3,4-dihydro-2(1*H*)-naphthalenone (4). Sodium borohydride (1.05 g, 0.028 mol) was suspended in 25 mL of anhydrous diglyme and stirred while the mixture was cooled in an ice bath. 2-Methyl-2-butene (5.1 g, 0.073 mol) in 5 mL of diglyme was added. Freshly distilled boron trifluoride ethereate (5.3 g, 0.037 mol) was added over a 30-min period. After the mixture had been stirred in an ice bath for 3 h, a solution of hydrocarbon 1 (5.1 g, 0.016 mol) in 5 mL of diglyme was added over a 15-min period. The reaction mixture was allowed to come to room temperature and stirred for 19 h. It was then cooled in ice, and 7 mL of 3 N sodium hydroxide solution was added. 30% Hydrogen peroxide solution (15 mL) was added over a 45-min period, with the temperature being kept below 8 °C. Water was then added, the mixture was extracted with ether, and the ether solution washed six times with 200-mL portions of water. It was then dried over magnesium sulfate, and the solvent was evaporated. The residual oil was dissolved in 55 mL of acetone, and the solution was cooled in ice. A solution containing 1.125 g (0.0125 mol) of chromium(VI) trioxide, 10 mL of concd sulfuric acid, and 3 mL of water was added over a 10-min period, maintaining the temperature below 5 °C. The ice bath was then removed, and the solution was allowed to stand for an additional 20 min, after which water was added. The mixture was extracted with ether, and the organic layer was washed twice with water, dried over magnesium sulfate, and evaporated. The residual brown oil was chromatographed on neutral alumina (activity III), eluting with 15% methylene chloride in pentane, to give ketone 4 (2.9 g, 0.009 mol, 57%) as a colorless oil: ^{1}H NMR δ 2.58 (s, 2 H), 3.00 (d, J = 13.4 Hz, 2 H), 3.13 (s, 2 H), 3.25 (d, J = 13.4 Hz, 2 H), ca. 7.2 (m, 14 H); IR ν_{max} 1715, 1263, 911, 762, 747, 701 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O$: C, 88.30; H, 6.79. Found: C, 88.40; H, 7.01.

Reaction of 4 with Phosphorus Pentabromide. Phosphorus pentabromide (6.7 g, 0.0156 mol) in 30 mL of methylene chloride was stirred and cooled in an ice bath. A solution of ketone 4 (2.0 g, 0.0061 mol) in 10 mL of methylene chloride was added over a period of 10 min. The ice bath was then removed, and the solution was stirred for 3 h and then poured onto crushed ice. The organic layer was separated, washed with dilute sodium hydroxide solution, and then with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated to yield a viscous brown oil. Chromatography on silica gel, eluting with a 1:1 mixture of methylene chloride and petroleum ether, followed by recrystallization from ethanol yielded 1-bromo-3,4-dibenzyl-2-naphthol (1.4 g, 0.0035 mol, 57%) as a pale yellow solid: mp 141–142 °C; ^{1}H NMR δ 4.29 (s, 2 H), 4.43 (s, 2 H), 6.07 (s, 1 H), 7.16 (m, ca. 10 H), ca. 7.2–7.55 (m, ca. 2 H), 7.92 (dd, J = 10.1, 1.9 Hz, 1 H), 8.11 (dd, J = 8.0, 1.9 Hz, 1 H); IR (KBr) ν_{max} 3420, 1598, 1499, 1455, 1449, 1371, 1326 cm^{-1}. Anal. Calcd for $C_{24}H_{19}BrO$: C, 71.47; H, 4.75; Br, 19.81. Found: C, 71.29; H, 4.91; Br, 19.98.

Reaction of Bromine with 4. A solution of bromine (0.54 g, 3.34 mmol) in 1 mL of carbon tetrachloride was added to a solution of ketone 4 (0.55 g, 0.17 mmol) in 5 mL of carbon tetrachloride. The solution was shaken briefly and allowed to stand at room temperature for 15 min, after which the bromine color had disappeared. The solution was washed with sodium bicarbonate solution and then with water and dried over magnesium sulfate, and the solvent was evaporated under vacuum, maintaining the temperature below 30 °C, to give 0.81 g of yellow oil. Its NMR spectrum showed peaks at δ 2.71 (s), 3.04 (d, J – 13 Hz), and 3.29 (d, J = 13 Hz) as well as aromatic peaks. On standing at room temperature for several weeks, or on attempted chromatography on alumina or silica, the product was largely converted to phenol 10.

3,4-Dibenzyl-2-naphthol (11). 1-Bromo-3,4-dibenzyl-2-naphthol (0.40 g, 0.95 mmol) was dissolved in 2 mL of glacial acetic acid, and the solution was heated on a steam bath while zinc dust (0.65 g, 0.01 mol) was added over a 0.5-h period. Heating was continued, with occasional stirring, for an additional hour. The mixture was then poured into water and extracted with methylene chloride. The organic layer was filtered free of zinc dust, washed with water and then sodium bicarbonate solution, dried over magnesium sulfate, and filtered, and the solvent was evaporated. The residue was chromatographed on silica gel, eluting with 1:1 pentane–methylene chloride, to yield phenol 11 as a pale yellow oil (0.21 g, 0.65 mmol, 68%): ^{1}H NMR δ 4.21 (s, 2 H), 4.41 (s, 2 H), 6.59 (s, 1 H), ca. 7.0 (6.8–7.1) (m, ca. 12 H), ca. 7.2–7.4 (m, ca. 2 H); IR (mineral oil) ν_{max} 3532 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O$: C, 88.88; H, 6.22. Found: C, 89.14; H, 5.99.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work. We also thank Professor Roberta Day for X-ray crystallographic analysis and Professor Paul Lahti for assistance with the Molecular Mechanics program.