Formation and Rearrangement of 8a-Benzyl-2-*tert*-butyl-1(8a*H*)-naphthalenone, a Ketone with a Ring System Consisting Entirely of Fused Blocked Aromatic Rings

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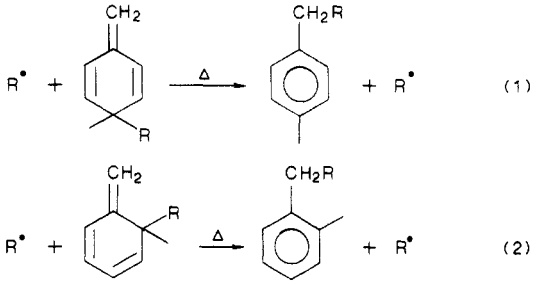
The dibromobicyclic ketone **5** was synthesized by a three-step process starting with 2-*tert*-butyl-1-naphthol. Dehydrobromination of **5** by reaction with DBU resulted in isolation of the 1-naphthalenone **7**. Formation of **7** is attributed to a [1,5] shift in the intermediate ketone **3**. This reaction provides the first evidence for formation of a molecule with a ring system consisting entirely of fused blocked aromatic rings.

Semibenzenes (methylenecyclohexadienes) and cyclohexadienones are the best known examples of "blocked aromatic molecules", in which the presence of a single quaternary carbon in a six-membered ring prevents the molecule from isomerizing to a more stable aromatic structure. Semibenzenes normally rearrange rapidly via free radical chain processes (the "semibenzene rearrangement", eq 1 and 2),[1] except when [3,3] migrations



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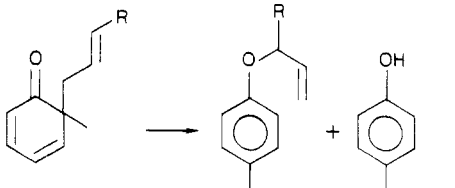
of the blocking groups will immediately yield aromatic structures.[1j] Cyclohexadienones undergo a wide and rather bewildering variety of rearrangements in acid.[2] On heating in the absence of acids, however, they undergo principally allowed, concerted rearrangement processes, such as those shown in eq 3 and 4.[2]



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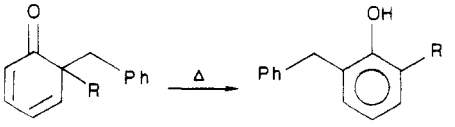

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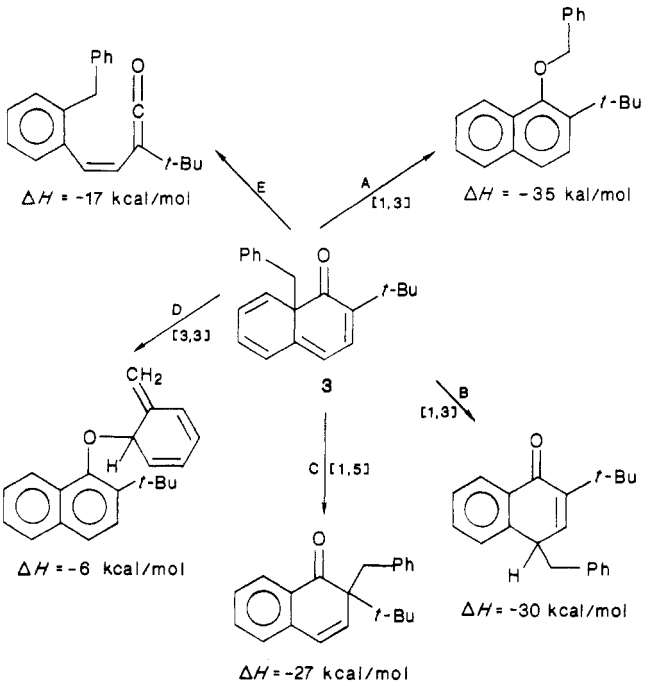
Molecules containing *fused* blocked aromatic rings, in which the presence of a single blocking group could prevent the simultaneous aromatization of two (or more) blocked aromatic rings, would have exceptionally high driving forces for rearrangement.

Scheme I



Only two examples of molecules containing fused blocked aromatic rings have thus far been characterized in the literature. These compounds (ketone **1**,[3] containing fused semibenzene and cyclohexadienone rings, and hydrocarbon **2**,[4] containing two fused semibenzene rings) are

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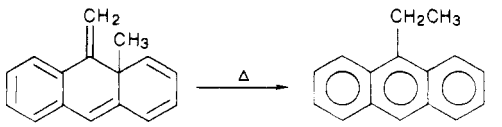


2

atypical fused blocked aromatic molecules because the presence of the fused benzo groups greatly decreases the driving forces for "double aromatization" of the two nonaromatic rings. Thus, relatively high temperatures are required for their rearrangements. However, hydrocarbon **2** does undergo a novel thermal "double aromatization"

(1) (a) von Auwers, K.; Keil, G. *Chem. Ber.* **1903**, *36*, 1861. (b) von Auwers, K. *Justus Liebigs Ann. Chem.* **1907**, *352*, 219. (c) von Auwers, K.; Juhlicher, W. *Chem. Ber.* **1922**, *55*, 2167. (d) Fuson, R. C.; Miller, T. G. *J. Org. Chem.* **1952**, *17*, 316. (e) Tse, R. L.; Newman, M. S. *Ibid.* **1956**, *21*, 638. (f) Bird, C. W.; Cookson, R. C. *Ibid.* **1959**, *24*, 441. (g) Hart, H.; DeVrieze, J. D. *Tetrahedron Lett.* **1968**, 4259. (h) Newman, M. S.; Layton, R. M. *J. Org. Chem.* **1968**, *33*, 2338. (i) Miller, B.; Lai, K.-H. *J. Am. Chem. Soc.* **1972**, *94*, 3472. (j) Miller, B.; Saidi, M. R. *Ibid.* **1976**, *98*, 2544.

(2) Miller, B. *Acc. Chem. Res.* **1975**, *8*, 245.

(3) Miller, B.; Bhattacharya, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 3234.

(4) Miller, B.; Bhaghdachi, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1257.

0022-3263/87/1952-3390$01.50/0

process, possibly via a radical dissociation–recombination process.[4]

In this paper we report evidence for the synthesis and rearrangement of ketone **3**, whose ring skeleton consists solely of fused blocked aromatic (semibenzene and cyclohexadienone) rings.[5]

We anticipated that the benzylic blocking group in **3** might undergo at least five reasonable exothermic migrations. These possibilities are illustrated in Scheme I. Only the initial migration steps and the enthalpy values calculated for those steps[6] are illustrated in the Scheme. Obviously, the products of processes B and D would aromatize easily, while the ketene which would form from process E should undergo a second electrocyclic reaction (in nonnucleophilic solvents) to form, eventually, 5-benzyl-2-*tert*-butyl-1-naphthol.[7]

All processes shown in Scheme I would be highly exothermic, and it is difficult, a priori, to select the most probable path. However, the most exothermic reactions, A and B, are forbidden to occur as concerted, suprafacial processes[8] and would presumably proceed by radical chain mechanisms. (Reaction B is a semibenzene rearrangement, and reaction A could proceed via an analogous, though novel, mechanism.)

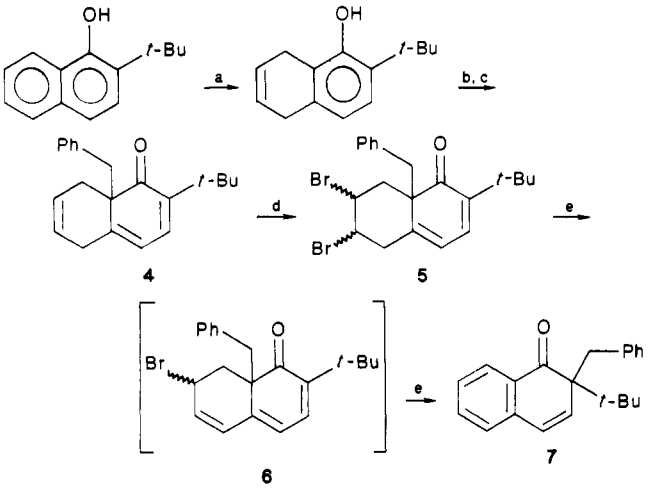
The [1,5] benzyl shift in process C is analogous to known reactions of other cyclohexa-2,5-dien-1-ones.[2,9] However, the temperatures required for those rearrangements are significantly higher than the temperatures required for benzyl group shifts in semibenzene rearrangements.[1i,j]

Reverse Claisen migrations of allyl groups in cyclohexadienones (eq 3) proceed at temperatures significantly lower than those required for [1,5] benzyl shifts.[2] However, reverse Claisen migrations of benzyl groups have never been observed, since the initial steps would be very endothermic. Rearrangement of **3** by reaction D would be a unique example of an exothermic reverse Claisen rearrangement of a benzyl group.

Finally, process E would proceed via electrocyclic ring opening of the cyclohexadienone ring. Electrocyclic ring openings of cyclohexa-1,3-dienes proceed far more rapidly than [1,5] or [3,3] shifts in thermal reactions of unstrained hydrocarbons.[11] However, ring openings of cyclohexadienones to form ketenes would be highly endothermic processes. Thus, while such ring openings are common photochemical processes, they have not been observed to occur under thermal conditions. Since the ring opening process in **3** would be an exothermic reaction, it would be of interest to see whether it would be more rapid than the various possible rearrangement processes.

Synthesis of the Fused Blocked Aromatic Ketone 3. We proposed to prepare the carbon skeleton of **3** by carrying out a Claisen alkylation on a 1-hydroxytetralin derivative and then introducing additional double bonds to form the semibenzene ring. However, Claisen alkylation of 1-hydroxytetralin or of its $\Delta^{6,7}$ derivative would almost certainly occur predominantly at the unsubstituted ortho position of the phenolic ring rather than at the ring juncture. Therefore, a phenol substituted by a *tert*-butyl group at the ortho position was chosen as the starting material (Scheme II).

Scheme II[a]



[a] (a) Li, NH_3; (b) *n*-BuLi; (c) $PhCH_2Br$, 25 °C, 19 h; (d) Br_2, 0.1 mol of NBS; (e) DBU, 0 °C.

Birch reduction of 2-*tert*-butyl-1-naphthol followed by Claisen benzylation thus yielded the bicyclic ketone **4**. (The *tert*-butyl group at C-2 not only directs alkylation to the ring junction, but minimizes possible problems with Diels–Alder condensations of **4** and later products containing cyclohexadienone rings.)

Having obtained ketone **4**, it was only necessary to introduce one additional double bond to prepare the desired fused blocked aromatic ketone **3**. Initial attempts to accomplish this by NBS bromination of **4**, followed by dehydrohalogenation, foundered when complex mixtures were obtained from the NBS reactions. One equivalent of bromine was therefore added to a solution of **4** in CCl_4 solution at 0 °C. Despite the mild conditions, HBr fumes appeared during the addition of bromine. The resulting reaction mixture, after a washing with water and evaporation of the solvent, included no components containing carbonyl groups. Instead, chromatography yielded benzyl bromide (56%) and phenolic products including 2-*tert*-butyl-5,8-dihydro-1-naphthol (6%), 2-*tert*-butyl-1-naphthol (34%), and 4-bromo-2-*tert*-butyl-1-naphthol (11%).

It seemed likely that the processes leading to these products were catalyzed by the acid produced during the reaction, so we decided to carry out addition of bromine to **4** under conditions in which the formation and accumulation of HBr would be minimized. The results of an initial experiment in which 2,6-di-*tert*-butylpyridine was added to the reaction mixture before bromination did not look encouraging, so the use of NBS as an HBr absorber was investigated. When the reaction was carried out as before except that 12 mol % of NBS was added to the reaction mixture before bromination there were no obvious signs of HBr formation. Evaporation of the solvent at low temperature followed by rapid chromatography on Florisil at 0 °C gave the desired dibromide **5** in 44% yield. Ketone **5** is a sensitive compound which eliminates HBr on heating above 50 °C and, in some runs, on chromatography on silica gel. However, it appeared to be stable for several weeks in the refrigerator.

To eliminate HBr from ketone **5**, 2 equiv of DBU were added to a solution of the ketone in CCl_4 solution at 0 °C. The reaction was monitored by UV. A peak at 378 nm, which was attributed to the monodehydrobromination

(5) A preliminary report of this work has been published: Miller, B.; Baghdadchi, J. *J. Chem. Soc., Chem. Commun.* **1986**, 511.

(6) Values for enthalpy changes were calculated by using group values from: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(7) Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 500.

(8) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1971.

(9) Miller, B.; Lai, K.-H. *Tetrahedron Lett.* **1972**, 517.

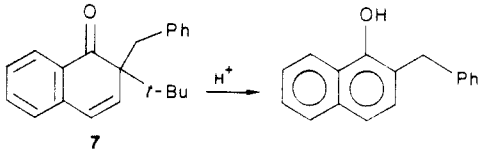
(10) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103.

(11) Kropf, P. J. "Photochemical Transformations of Cyclohexadienones and Related Compounds" In *Organic Photochemistry*; Chapman, O., Ed.; Marcel Dekker: New York, 1967; Vol. 1.

product **6**, appeared quickly, and reached maximum intensity after ca. 10 min. The 378-nm peak gradually faded and was essentially gone after 18 h. (Attempts in other runs to isolate **6** by column chromatography or preparative TLC failed.)

Observation over the first 5 h of the reaction, or at the end of the reaction, showed no long wavelength absorption (λ_{max} >400 nm) which could be attributed to the blocked aromatic ketone **3**. In a second reaction, *N*-phenylmaleimide was added before introduction of DBU, in the hope of trapping ketone **3** as its Diels-Alder adduct. No evidence for formation of such an adduct could be detected.

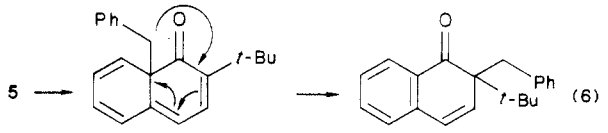
After 18 h, thin-layer chromatographic analysis of the first reaction mixture indicated the presence of a single principal product. Flash chromatography on silica gel yielded a bromine-free product. Its IR and UV spectra, as well as its NMR spectrum, which showed the presence of a benzyl group bonded to a chiral center and a single nonaromatic double bond, probably bonded to an aromatic ring, were consistent with structure **7** for this compound. This structural assignment was supported by the observation that addition of sulfuric acid to a solution of **7** in acetic acid rapidly resulted in loss of the *tert*-butyl group from **7** to form 2-benzyl-1-naphthol (eq 5). The loss of *tert*-butyl groups from quaternary carbons of linearly conjugated cyclohexadienones has frequently been observed during studies of acid-catalyzed dienone–phenol rearrangements.[12]



7 (5)

Discussion

Our attempts to detect the presence of the fused blocked aromatic ketone **3** were unsuccessful. However, it is difficult to find a reasonable mechanism for the formation of naphthalenone **7** other than by a migration of the benzyl group in **3** (eq 6). Neither **4** nor **5** undergoes a similar rearrangement at these temperatures in the absence of DBU, and there seems no reason to believe that DBU would catalyze the benzyl shift.



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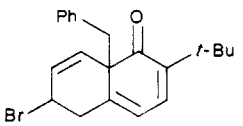
Although the UV spectrum of the reaction mixture suggests that, as expected, the initial dehydrobromination product of **5** is **6**, it is conceivable that a small amount of **8** may be initially formed in that reaction. Since the



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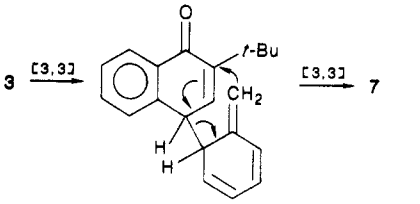
C–benzyl bond in **8** is weaker than that in **4** or **5**, **8** may be somewhat more prone to rearrangement. However, comparison with the rates of thermal benzyl shifts in other cyclohexadienones (see below) suggests that it is very unlikely that a similar shift in **8** would take place at 0 °C.

The formation of **7** by dehydrobromination of **5** thus provides strong evidence for the intermediate formation of the fused blocked aromatic ketone **3**.

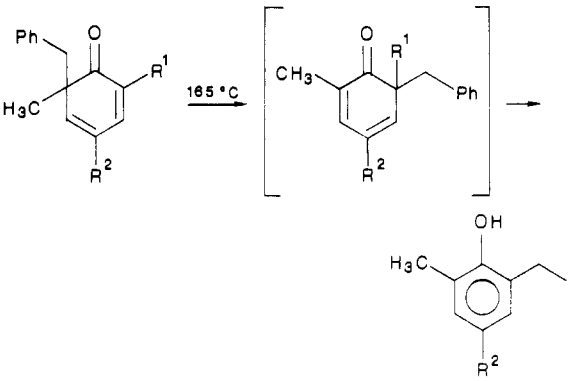
Rearrangement of **3** is depicted in eq 6 as proceeding by a single [1,5] shift. The product, **7**, might formally be obtained by a sequence of [3,3] shifts of the benzyl group (eq 7), as suggested by a referee. In contrast to the highly



(7)

exothermic [1,5] shift, however, the initial [3,3] shift would be endothermic by ca. 10 kcal/mol.[6] Furthermore, it seems probable that the initial rearrangement product would tautomerize rapidly to a phenol in the presence of DBU. Thus, rearrangement of **3** by a single [1,5] shift appears more plausible.

The rearrangement of **3** to **7** is so rapid, at room temperature or below, that the intermediate **3** cannot be detected even by the very sensitive UV probe. In contrast, cyclohexadienone **9a** requires a half-life of more than 3 h to undergo rearrangement at 165 °C (eq 8). Ketone **9b**, lacking the *tert*-butyl group at the migration terminus, rearranges only slightly more rapidly ($t_{1/2} \simeq 1$ h).[13]



(8)

9a, R^1 = *t*-Bu, R^2 = H
9b, R^1 = H, R^2 = *t*-Bu

The very rapid rate of rearrangement of **3** in comparison to that of **9** is readily understandable, since rearrangement of **3** proceeds with formation of a new aromatic ring, while the initial step in rearrangement of **9** simply converts one nonaromatic ring to another. This reaction provides a dramatic demonstration of the effect of the fused blocked aromatic structure of **3** on its reactivity.

The rearrangement of ketone **3** to **7** proceeds via the most exothermic of the suprafacial, concerted paths shown in Scheme I. It is clear that **7** was indeed formed via a concerted migration, since reaction via dissociation to free radicals would certainly have led to formation of the benzyl naphthyl ether or the 4-benzylnaphthol rather than to **7**.

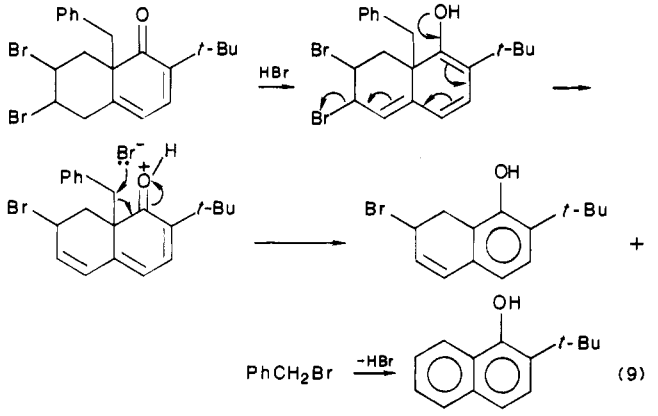
The fact that radical chain paths leading to these products do not occur seems inconsistent with previous observations that semibenzene rearrangements involving migrations of benzyl groups[11] occur at much lower temperatures than do [1,5] benzyl shifts in cyclohexadienones.[13] It is difficult to be sure of the significance of the absence of semibenzene rearrangement products,

(12) (a) Miller, B.; Margulies, H. *J. Am. Chem. Soc.* **1965**, *87*, 5106. (b) Miller, B. *Ibid.* **1970**, *92*, 6252.

(13) Lai, K. H. Ph.D. Dissertation, University of Massachusetts, Amherst, 1971.

since the possible presence of adventitious traces of inhibitors or initiators may greatly affect the rates of semibenzene rearrangements.

We have considered the possibility that the formation of 2-*tert*-butyl-1-naphthol during addition of bromine to **4** may have proceeded, in part, via acid-catalyzed fragmentation of the fused blocked aromatic ketones **3**. However, dehydrobromination of **5** to **3** seems unlikely to have occurred in the absence of base, and the simultaneous formation of 2-*tert*-butyl-5,8-dihydro-1-naphthol in that reaction demonstrates that **3** is not a *necessary* intermediate for the fragmentation process. We suggest that fragmentation occurs by the mechanism shown in eq 9.



(9)

It is noteworthy that only fragmentation and not rearrangement products are obtained, although ketone **9a** undergoes principally rearrangement in acetic acid–sulfuric acid solutions.[12b] This difference can be attributed to the high nucleophilicities of bromide ions in non-hydrogen-bonding solvents.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were recorded on a Perkin-Elmer 202 spectrometer in methanol solution, unless otherwise indicated. Infrared spectra were recorded on a Perkin-Elmer 237B or 1310 spectrometer. Only major peaks are reported. ^{1}H nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R12 or Varian XL300 spectrometer. ^{13}C nuclear magnetic resonance spectra were recorded on the Varian XL300 instrument. Low-resolution mass spectra were obtained with a Perkin-Elmer-Hitachi RMUGL instrument. Microanalyses were carried out by the University of Massachusetts Microanalytical Laboratory.

2-*tert*-Butyl-5,8-dihydro-1-naphthol. Lithium metal (2.80 g, 0.40 mol) was cut into small pieces and added to ca. 500 mL of liquid ammonia in a three-necked flask fitted with a mechanical stirrer, gas inlet, and dry ice condenser. The mixture was stirred under argon for 30 min. A solution of 2-*tert*-butyl-1-naphthol (8.0 g, 0.040 mol) in 50 mL of anhydrous ether was added over a 10-min period and the solution stirred for an additional 45 min. Absolute ethanol (80 mL) was then added over a 30-min period. The solution was stirred and the ammonia evaporated under a stream of argon overnight. Water (800 mL) was added, and the mixture was extracted with four 150-mL portions of ether. The ether extracts were washed with 1 M hydrochloric acid solution, with brine, and with water and dried over anhydrous potassium carbonate. Evaporation of the solvent yielded 8.2 g of a dark yellow oil, which solidified on standing. Recrystallization from pentane yielded 2-*tert*-butyl-5,8-dihydro-1-naphthol (6.21 g, 0.031 mol, 76%) as colorless crystals: mp 68–68.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9 H), 3.11 (m, 2 H), 3.23 (m, 2 H), 4.75 (s, 1 H, O*H*), 5.91 (s, 2 H), 6.64 (d, J = 8.5 Hz, 1 H), 7.13 (d, J = 8.5 Hz, 1 H); IR (mineral oil) 3610 (w), 3559, 1422, 1222, 1126, 979, 801 cm^{-1}; mass spectrum, m/e 202 (M^+), 201 ($M^+ - 1$), 187 ($M^+ - 15$). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.04; H, 9.09.

8a-Benzyl-2-*tert*-butyl-5,8-dihydro-1(8a*H*)-naphthalenone (4). A solution of 1.51 M *n*-butyllithium (6.5 mL, 9.82 mmol) in hexane was added to a stirred solution of 2-*tert*-butyl-5,8-dihydro-1-naphthol (1.82 g, 9.01 mmol) in 100 mL of anhydrous benzene. The resulting suspension was stirred for an additional 45 min, and benzyl bromide (1.73 g, 10.1 mmol) was added via a hypodermic syringe. The yellow suspension was stirred at room temperature for an additional 19 h. Water (ca. 500 mL) was added, the two layers were separated, and the aqueous layer was extracted with three 100-mL portions of ether. The combined organic layers were washed with water and with brine and dried over anhydrous potassium carbonate. Evaporation of the solvent on a rotary evaporator gave 2.2 g of a brown oil, which was subjected to flash chromatography on silica gel. Elution with 5% dichloromethane in hexane yielded 0.51 g of the desired ketone. Recrystallization from pentane gave pure **4** (0.45 g, 154 mmol, 17%) as colorless needles: mp 89–90.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9 H), 2.0–3.0 (m, ca. 4 H), 3.15 (d, J = 13.5 Hz, 1 H), 3.32 (d, J = 13.5 Hz, 1 H), 5.75–5.85 (m, 2 H), 6.08 (dd, J = 7.0, 2.0 Hz, 1 H)., 6.72 (d, J = 7.0 Hz, 1 H), 7.05–7.20 (m, 5 H); IR (neat) 1672, 1653, 1480, 1387, 742, 700 cm^{-1}; UV (CH_3OH) λ_{max} 325 nm (ϵ 3841). Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.11; H, 8.31.

Reaction of Ketone 4 with Bromine. A solution of bromine (0.62 g, 3.88 mmol) in 10 mL of dry carbon tetrachloride was added over a 5-min period to a stirred solution of ketone **4** (1.18 g, 4.0 mmol) in 20 mL of dry carbon tetrachloride. The reaction mixture was maintained between −5 and 0 °C. Hydrogen bromide vapors began to appear above the surface of the solution after addition of about one-half of the bromine. Stirring was continued for 5 min after addition of the bromine was complete and the reaction mixture then poured into a mixture of ice and aqueous sodium bicarbonate solution. The carbon tetrachloride layer was washed with water and dried over magnesium sulfate and the solvent evaporated on a rotary evaporator under vacuum to yield 1.4 g of orange oil, whose IR spectrum showed no significant carbonyl peaks. Flash chromatography on silica gel, eluting with 5% ethyl acetate in pentane, yielded benzyl bromide (0.37 g, 56%) and a mixture of phenolic materials, which were subjected to a second chromatography. Elution with the same solvent yielded **2-*tert*-butyl-5,8-dihydro-1-naphthol** (0.048 g, 6%), **2-*tert*-butyl-1-naphthol** (0.27 g, 35%), and **4-bromo-2-*tert*-butyl-1-naphthol** (0.123 g, 11%).

4-Bromo-2-*tert*-butyl-1-naphthol. A solution of bromine (0.8 g, 5.0 mmol) in 2 mL of glacial acetic acid was added to a solution of 2-*tert*-butyl-1-naphthol (1.0 g, 5.0 mmol) in 5 mL of acetic acid. After 5 min the solution was diluted with water and extracted with dichloromethane. The organic layer was washed with water, with sodium bicarbonate solution, and again with water and dried over magnesium sulfate. Evaporation of the solvent left 1.4 g of brown solid, which was recrystallized from hexane to yield 4-bromo-2-*tert*-butyl-1-naphthol (0.90 g, 3.2 mmol, 64%) as cream colored needles: mp 69–71 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 9 H), 4.64 (s, 1 H, O*H*), 7.70–7.90 (m, 2 H), 8.05 (s, 1 H), 8.05–8.23 (m, 2 H); IR (mineral oil) 3520, 1620, 1301, 1247, 874, 772, 732 cm^{-1}. Anal. Calcd for $C_{14}H_{15}OBr$: C, 60.23; H, 7.42; Br, 28.63. Found: C, 59.99; H, 5.39; Br, 28.82.

8a-Benzyl-2-*tert*-butyl-6,7-dibromo-5,6,7,8-tetrahydro-1-(8a*H*)-naphthalenone (5). A solution of ketone **4** (0.85 g, 2.91 mmol) and *N*-bromosuccinimide (0.067 g, 0.38 mmol) in 10 mL of dry carbon tetrachloride was stirred and cooled to −5 °C in an ice–salt bath. A solution of bromine (0.45 g, 2.81 mmol) in 5 mL of dry carbon tetrachloride was cooled to 0 °C and added drop by drop, over a 6-min period, to the ketone solution. Absorption of bromine was rapid, and a bright yellow solution was obtained immediately after completion of the addition. A mixture of aqueous sodium sulfite, sodium bicarbonate, and ice was added to the stirred reaction mixture, and the organic layer was separated, washed with cold water, and dried over anhydrous sodium sulfate. The flask was kept in a refrigerator during drying. The mixture was filtered and the solvent evaporated under vacuum at 20 °C to yield 1.3 g of orange oil. The product was subjected to chromatography on Florisil in a column surrounded by ice, eluting with 5% ethyl acetate in petroleum ether. Solvent was evaporated under vacuum with the temperature kept at room temperature or below to yield ketone **5** (0.57 g, 1.26 mmol, 44%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 9 H), 1.6–1.7 (m, ca. 2 H), 2.5–2.7 (m, ca. 2 H), 3.13 (d, J = 13 Hz, 1 H), 3.90 (d, J = 13 Hz, 1 H), 4.55–4.75 (m, 1 H), 4.75–4.95 (m, 1 H), 6.10 (dd, J = 8.0, 1.5 Hz, 1 H), 6.69 (d, J = 8 Hz, 1 H), 7.06–7.25 (m, 5 H);

IR (neat, major peaks) 1676, 1655, 1625 (w), 1350, 1021, 905, 733, 695 cm^{-1}; UV (methanol) λ_{max} 327 nm (ϵ 4010). Anal. Calcd for $C_{21}H_{24}OBr_2$: C, 55.76; H, 5.35; Br, 35.33. Found: C, 55.42; H, 5.36; Br, 35.53.

2-Benzyl-2-*tert*-butyl-1-naphthalenone (7). A solution of ketone **5** (0.34 g, 0.75 mmol) in 10 mL of dry carbon tetrachloride was cooled to 0 °C and stirred while 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.30 g, 1.97 mmol) was added rapidly. The deep yellow solution was stirred at 0 °C for 5 h and then allowed to warm to room temperature while stirring was continued for an additional 13 h. Dichloromethane (25 mL) was added to the resulting mixture, which was cooled in ice, washed with water, with a mixture of 0.01 M hydrochloric acid and ice, and again with water, and dried over magnesium sulfate. The solvent was evaporated under vacuum to give 0.26 g of a brown oil, which was chromatographed on silica gel, eluting with 5% dichloromethane in petroleum ether. Ketone **7** (0.15 g, 0.53 mmol, 70%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 2.80 (d, J = 13.0 Hz, 1 H), 3.73 (d, J = 13.0 Hz, 1 H), 6.21 (d, J = 10.5 Hz, 1 H), 6.50 (d, J = 10.5 Hz, 1 H), 7.0–7.2 (m, 3 H), 7.95 (dd, J = 7.5, 1.5 Hz, 1 H). IR (neat) 1685, 1676, 1601, 1463, 1385, 1298, 1196, 693 cm^{-1}; UV (methanol) λ 239 (ϵ 35 147), 274 (6759), 336 (3714) nm. Anal. Calcd for $C_{21}H_{22}O$: C, 86.84; H, 7.64. Found: C, 86.81; H, 7.80.

Reaction of 7 with Acid. Concentrated sulfuric acid (one drop) was added to a solution of ketone **7** (0.048 g, 0.166 mmol) in 2 mL of glacial acetic acid. The solution was allowed to stand at room temperature for 5 min and then poured into a mixture of water (50 mL) and dichloromethane (25 mL). The organic layer was separated, washed with water and with sodium bicarbonate solution, and dried over magnesium sulfate. Evaporation of the solvent left 0.4 g of dark brown oil, which crystallized on seeding with a sample of 2-benzyl-1-naphthol which had been prepared by Claisen alkylation of 1-naphthol. Recrystallization from petroleum ether yielded 0.024 g (0.01 mmol, 62%) of 2-benzyl-1-naphthol, mp 72–73 °C (lit.[14] mp 73–74 °C).

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Registry No. **4**, 103768-73-6; **5**, 103768-74-7; **7**, 103768-75-8; 2-*tert*-butyl-1-naphthalenol, 27286-81-3; 2-*tert*-butyl-5,8-dihydro-1-naphthalenol, 103768-72-5; 4-bromo-2-*tert*-butyl-1-naphthalenol, 108744-28-1; 2-benzyl-1-naphthalenol, 36441-32-4.

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4-Bromo-2-sulfolenes. Butadienyl Cation Equivalents

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4-Bromo-2-sulfolene and 4-bromo-3-methyl-2-sulfolene react with alkylcuprates to give direct substitution products, with vinyl- or phenylcuprates or sulfur-containing nucleophiles to give allylic substitution products, and with strongly basic nucleophiles to give elimination products. The allylic substitution products and the isomerized direct substitution products are precursors for substituted 1,3-butadienes. Thus, these 4-bromo-2-sulfolenes serve as butadienyl cation equivalents.

1,3-Butadiene is a commonly occurring functionality in natural products. The use of substituted 1,3-butadienes in Diels–Alder reactions is a major route toward the formation of complex cyclic molecules. Therefore, the preparation of functionalized 1,3-butadienes is an important task in organic synthesis. Recently,[1] there has been an increasing interest in studying the deprotonation/substitution reactions of 3-sulfolenes for the preparation of the stable precursors for alkylated,[1a,b] acylated,[1c] and silylated[1d] 1,3-butadienes and their application in the synthesis of natural products.[1e,f] The advantages of this strategy include the preparation reaction being essentially one step, the moderately unstable dienes being produced in their protected forms, the substitution step being regioselective, and the SO_2 extrusion reaction step being stereospecific. However, since this approach is limited to attaching electrophiles to the 1- or 4-positions of conjugated dienes, it is desirable to have butadienyl cation equivalents where nucleophiles can be introduced so that more differently functionalized 1,3-butadienes can be synthesized.

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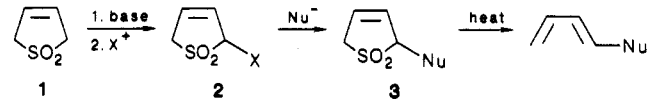
Scheme I[a]



It was considered that the introduction of a potential leaving group such as a halide or a sulfide at the α-position of 3-sulfolene (**1**) would yield an electrophilic sulfolene **2** that, upon treatment with a nucleophile, should give the α-substituted product **3**. However, attempts at the preparation of **2** were unsuccessful. The reactions of 3-sulfolene anion with *N*-bromosuccinimide, *N*-chlorosuccinimide, 1-chlorobenzotriazole, and diphenyl disulfide resulted in no reaction, while reactions with iodine, bromine, iodine chloride, and dimethyl disulfide gave complex mixtures. In no case were we able to identify the formation of the desired product **2** (Scheme I, X = halogen or sulfide).

We later found that 4-bromo-2-sulfolene (**4**),[2] available from 3-sulfolene (**1**) by a reaction sequence of bromine addition and partial dehydrobromination, could react with a variety of nucleophiles via different routes (Scheme II). The reaction of **4** with methylcuprate (from methyllithium and CuI) or *n*-butylcuprate (from butyllithium and CuI) proceeded in an allylic substitution reaction mode, giving 2-alkylated 3-sulfolenes **5** and **6**, respectively. The reaction

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