solution) was added. The water layer was removed with a syringe. The NMR spectrum indicated that the threo diastereomer had formed exclusively. The ^{2}H-decoupled ^{1}H spectrum exhibits a doublet (J = 3.6 Hz) at 6.74 ppm upfield from internal benzene. The ^{1}H-decoupled ^{2}H spectrum exhibits two broad singlets at 6.74 and 6.17 ppm, respectively, from internal benzene-d_6. The absence of additional ^{1}H signals at 6.77 ppm (J = 13.3 Hz) indicates the absence of the erythro diastereomer (vide infra).

***erythro*-1,2-Dideuteriohexyl-9-BBN.** (*Z*)-1-Hexene-*1,2*-d_2 (1.5 mmol, 0.15 mL) was reacted with 9-BBN (1.5 mmol, 0.17 g) as described for the (*E*) diastereomer. NMR analysis indicated that only the erythro diastereomer was produced. The ^{2}H-decoupled ^{1}H spectrum exhibits a doublet (J = 13.3 Hz) at 6.77 ppm relative to internal benzene. The ^{1}H-decoupled ^{2}H spectrum consists of two broad singlets at 6.77 and 6.18 ppm relative to internal benzene-d_6. The absence of additional ^{1}H signals at 6.74 ppm (J = 3.6 Hz) indicates the absence of the threo diastereomer (vide supra).

Acknowledgment. The work at Clemson was supported, in part, by the National Institutes of Health (Grant No. 1-R01-GM22788-01) and the National Science Foundation (Grant No. CHE77-07808).

Registry No.—9-BBN, 280-64-8; $BH_3{\cdot}S(CH_3)_2$, 13292-87-0; 1-hexyne, 693-02-7; 1-hexyne-*1*-d_1, 7299-48-1; di(2-deuteriocyclohexyl)borane-*B*-d_1, 65253-16-9; dicyclohexylborane, 1568-65-6; cyclohexene, 110-83-8.

References and Notes

(1) (a) University of Tennessee; (b) Clemson University.
(2) H. C. Brown, "Organic Synthesis via Boranes", Wiley, New York, N.Y., 1975.
(3) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1973.
(4) C. M. L. Cragg, "Organoboranes in Organic Synthesis", Marcel Dekker, New York, N.Y., 1973.
(5) G. W. Kabalka, *Aldrichimica Acta*, **8**, 14 (1975).
(6) (a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959); (b) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).
(7) P. R. Jones, *J. Org. Chem.*, **37**, 1886 (1972).
(8) G. W. Kabalka and N. S. Bowman, *J. Org. Chem.*, **38**, 1607 (1973).
(9) D. E. Bergbreiter and D. P. Rainville, *J. Org. Chem.*, **41**, 3031 (1976).
(10) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).
(11) S. Bright, J. Platano, and J. Jacobus, *J. Org. Chem.*, **38**, 2554 (1973).
(12) D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6149 (1977).
(13) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974).
(14) J. A. Labinger, D. W. Hart, W. E. Seibert III, and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 3851 (1975).
(15) For Et_3B (Me_4Si reference), δ_{CH_3} 1.19 ppm and δ_{CH_2} 0.95 ppm, whereas for $Et_3B{\cdot}NMe_3$, δ_{CH_3} 0.78 ppm and δ_{CH_2} 0.32 ppm (H. Noth and H. Vahrenkamp, *J. Organomet. Chem.*, **12**, 23 (1968)).
(16) The products are racemic in each instance; for convenience, only a single enantiomer is illustrated.
(17) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963).
(18) In the ^{2}H decoupled ^{1}H spectrum, ^{11}B coupling ($^2J_{BH}$) is not observed; whether this is a consequence of the small magnitude of $^2J_{BH}$ or correlation decoupling,[12] or a combination of both factors, is currently unknown.
(19) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

Synthesis of 9,9-Dimethyl-2-methoxy-5-benzosuberone. An Unexpected Failure of Benzylic Oxidation

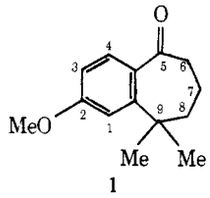
R. Bryan Miller* and Carlos G. Gutierrez

Department of Chemistry, University of California at Davis, Davis, California 95616

Received July 26, 1977

Attempts to prepare 9,9-dimethyl-2-methoxy-5-benzosuberone (1) by benzylic oxidation of 9,9-dimethyl-2-methoxybenzosuberan (9) proved unsuccessful. The problems associated with this oxidation are consistent with severe nonbonded interactions associated with the *gem*-dimethyl group in 9 which make formation of an initial benzylic radical difficult. Both nuclear magnetic resonance and ultraviolet data indicate a tendency of an sp^2-hybridized center adjacent to the aromatic nucleus in benzosuberans not to attain planarity with the phenyl ring, in contrast to the corresponding tetralin systems. An efficient synthesis of the ketone 1 from 4,4-dimethyl-6-methoxy-1-tetralone (3) is described.

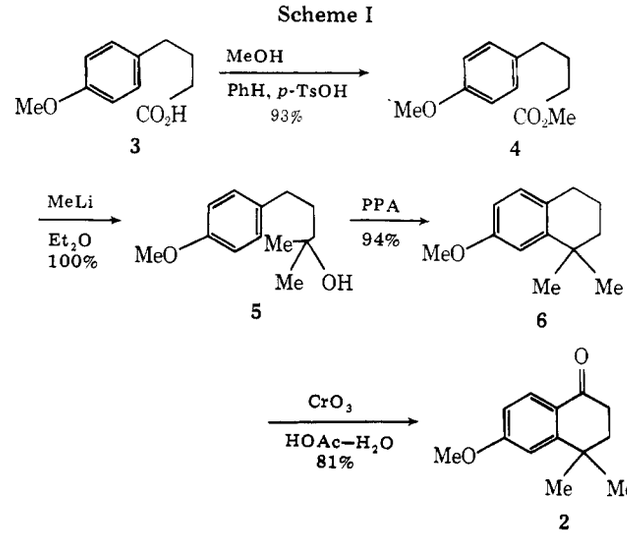
During a study of synthetic approaches to the himachalene class of sesquiterpenes,[1] 9,9-dimethyl-2-methoxy-5-benzosuberone (1) was a desired intermediate. Initial attempts to synthesize ketone 1 involved McMurry's ring expansion



1

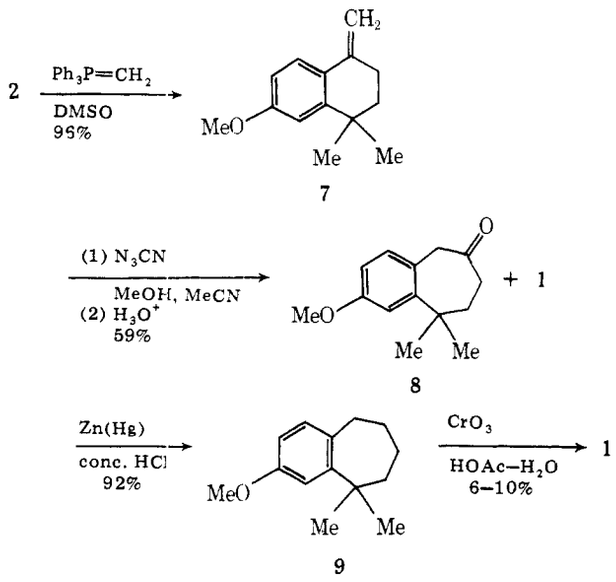
procedure[2] on 4,4-dimethyl-6-methoxy-1-tetralone (2) whose straightforward preparation is shown in Scheme I. For future consideration, it should be noted that the benzylic oxidation of tetralin 6 using chromium trioxide–acetic acid–water[3] proceeded in good yield. Treatment of tetralone 2 in dimethyl sulfoxide with methylenetriphenylphosphorane gave a 96% yield of the exocyclic olefin 7 which proved to be very labile.[4] Therefore, the crude exocyclic olefin 7 was subjected to cy-

Scheme I



0022-3263/78/1943-1569$01.00/0

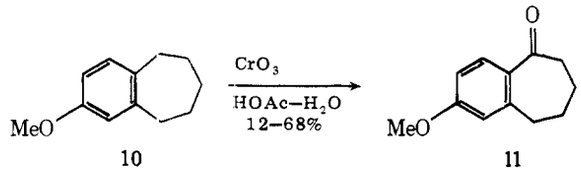
Scheme II



anogen azide ring expansion[2] to give a mixture of benzosuberones 8 and 1 (see Scheme II). The ratio of ketonic products 8 and 1 was found to be dependent on the method of preparation of the cyanogen azide solution.[5] If no precautions were taken to exclude sodium bromide (formed in situ by reaction of equimolar amounts of sodium azide and cyanogen bromide in acetonitrile) from the solution, the product distribution was 65:35 8/1.[6] However, if the cyanogen azide solution was filtered prior to use, the ratio shifted to 92:8 8/1.[6] Chromatography of the crude product obtained using the filtered cyanogen azide solution gave a 59% yield of the mixture of ketones 8 and 1. This mixture was subjected to Clemmensen reduction to give the benzosuberan 9 in 92% yield (see Scheme II).

Attempted benzylic oxidation of 9 → 1 with chromium trioxide–acetic acid–water in a similar manner to the successful oxidation of 6 → 2 resulted in poor mass recovery and only 6% yield of the desired ketone 1. Variation of reaction times, temperatures, and molar ratios gave an optimum yield of benzosuberone 1 of only 10%. Several other oxidative procedures also failed to give improved yields of ketone 1.[7]

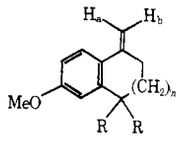
In order to determine whether the dramatic difference in the oxidation of tetralin 6 and benzosuberan 9 was due to the presence of the seven-membered ring or a combination of the seven-membered ring and the *gem*-dimethyl group, 2-methoxybenzosuberan (10)[8] was oxidized with chromium



10 11

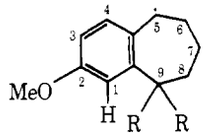
trioxide–acetic acid–water at 0 °C for 24 h, again the conditions used successfully for the transformation of 6 → 2. Examination of the reaction products revealed largely starting material and 12% of desired ketone 11. By optimizing the reaction conditions (28 h at room temperature) the yield of ketone 11 was raised to 68% (63% conversion).[9] When *gem*-dimethylbenzosuberan 9 was reacted under these conditions, a 10% yield of ketone 1 was obtained. Although this is higher than the 6% yield observed originally, the amount of starting material was very much reduced in the second case. The above observations indicate that a combination of the seven-membered ring and the *gem*-dimethyl group influence the yield in the benzylic oxidation but that the presence of the *gem*-dimethyl group is the dominant factor.

Table I. NMR Comparison of Exocyclic Olefins

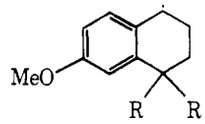


Compound	*n*	R	δ H_a, ppm	δ H_b, ppm
7	1	Me	5.21	4.75
15	2	Me	4.87	4.87
16	1	H	5.20	4.68
17	2	H	4.91	4.91

One explanation of these observations is that the benzylic radical, the initial species in the benzylic oxidation,[10] is more difficult to form in going from compounds 6 to 10 to 9. Resonance stabilization of the benzylic radical would be most effective if the carbon containing the odd electron were in the same plane as the phenyl ring, allowing for maximum overlap of the aromatic π system and the orbital bearing the lone electron. Examination of space-filling models of benzylic radical 12 where C-5 is assumed sp^2 hybridized and held rigidly in the plane of the aromatic ring shows a severe peri interaction between a C-9 methyl and a C-1 hydrogen. Holding the C-5 carbon in the aromatic plane also causes some torsional strain in the seven-membered ring. Inspection of models corresponding to radical 13, again holding the C-5 carbon rigid for maximum orbital overlap with the aromatic system, indicates that the C_9–H to C_1–H interaction is quite minimal. The main source of strain in this molecule is torsional, and this strain can be relieved if the C-5 carbon is not planar.[11] However, planarity can be easily attained if required. Models of radical 14 show it to be a relatively strain-free system.



12, R = Me
13, R = H

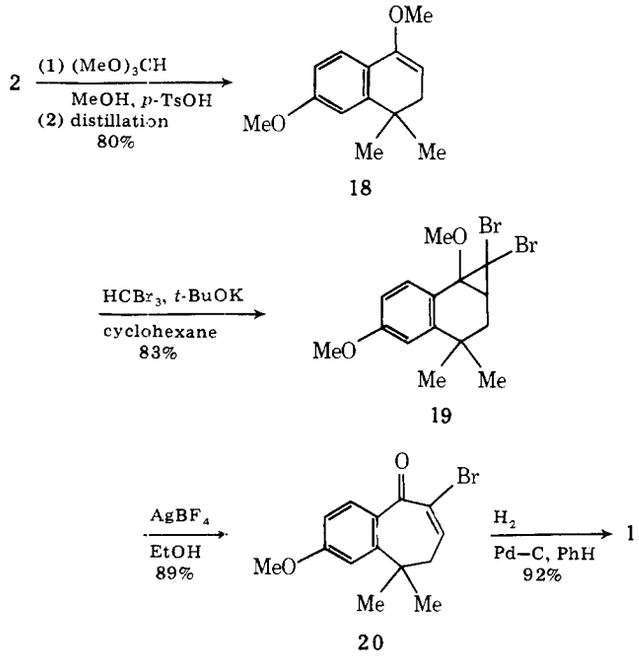


14

The tendency of an sp^2-hybridized center adjacent to the aromatic nucleus in benzosuberans *not* to attain planarity with the phenyl ring is consistent with an examination of the nuclear magnetic resonance spectra of compounds 7 and 15, and also 16[12] and 17 (see Table I). In the tetralin system 7, the two vinyl protons absorb at quite different fields due to H_a being in the deshielding portion of the induced magnetic field caused by the aromatic ring current while H_b is not.[13,14] In compound 15 the two exocyclic protons give rise to a single absorption at δ = 4.87 ppm, close to the δ = 4.80 ppm absorption for protons on an isolated exocyclic double bond on cyclohexane.[15] That H_a in compound 15 does not feel the diamagnetic anisotropic deshielding of the aromatic ring implies that the double dond and the phenyl nucleus are not in the same plane. Examination of space-filling models of this compound shows that indeed the double bond and the aromatic ring lie in intersecting planes with a substantial dihedral angle between them. Examination of the pair of compounds 16 and 17 shows a similar effect.

Further evidence that the exocyclic double bond in compound 15 is not coplanar with the aromatic ring is indicated from examination of its ultraviolet spectrum, which exhibits an absorption at 244 mμ (ε 8100) in 95% EtOH. This band appears at approximately 260 mμ in normal *p*-methoxystyrene systems.[16] The shift to shorter wavelength is consistent with

Scheme III



there being little π overlap between the exocyclic double bond and the phenyl nucleus in **15**. On the other hand, the ultraviolet absorption at 265 mμ (ϵ 13 700)[12] in 95% EtOH of compound **16** is consistent with the nuclear magnetic resonance data indicating that the exocyclic olefinic linkage in this compound is coplanar with the aromatic ring.

Our failure to functionalize the aromatic hydrocarbon **9** in any acceptable way forced us to look for an alternative route to benzosuberone **1** needed in our synthetic plan. An efficient solution to this problem is given in Scheme III.

Conversion of tetralone **2** to its methyl enol ether **18** was accomplished by treatment with methyl orthoformate and a catalytic amount of *p*-toluenesulfonic acid.[17] The crude reaction product was a mixture of dimethoxy ketal and enol ether **18**. However, distillation, during which the ketal underwent pyrolytic loss of methanol, afforded an 80% yield of the desired enol ether **18**. Addition of dibromocarbene to this olefin gave the crystalline tricyclic dibromocyclopropane **19**. The dibromocarbene was generated by either of two methods: (1) action of potassium *tert*-butoxide on bromoform in cyclohexane[17] or (2) use of 33% aqueous sodium hydroxide, bromoform, and Cetrimide (a phase reversal catalyst).[18] The yields of **19** were 83 and 69%, respectively, when the former and latter procedures were employed. The dibromide was ring expanded to bromoenone **20** in 89% yield by refluxing in ethanol in the presence of silver tetrafluoroborate.[19] Conversion of **20** to the much awaited benzosuberone **1** was accomplished in one step by concurrent saturation of the double bond and hydrogenolysis of the carbon–bromine bond by hydrogenation in benzene over palladium on charcoal catalyst using sodium carbonate to neutralize liberated hydrobromic acid. The transformation was accomplished in 92% yield. This scheme represents a 54% yield from tetralone **2** to benzosuberone **1**. It was found that when purification of intermediates, except enol ether **18**, was avoided an overall yield of 66% was obtained.

Experimental Section

Melting points are reported uncorrected. Boiling points were recorded at gauge pressure and are reported uncorrected. GLPC purifications are performed on a Varian Aerograph gas chromatograph Model 90P with 20% S.E.-30 on 60/80 Chrom WHDMS in a ¼ in. × 12 ft stainless steel column. Nuclear magnetic resonance spectra were recorded on either a Varian A-60A or Varian EM 360 instrument. Chemical shifts are reported in δ values (ppm) relative to tetramethylsilane as an internal standard. Infrared spectra were recorded on a Beckman IR-8 instrument, using polystyrene calibration points; only selected absorptions are reported. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer. Low resolution mass spectra were recorded on a Consolidated Electrodynamics Corporation mass spectrometer. High resolution mass spectra were determined by Mr. Kei Miyano on a Varian M-60 mass spectrometer. Analytical samples for high resolution mass spectroscopic analysis were prepared by preparative GLPC. Combustion analyses were determined by Chemalytics, Inc., Tempe, Ariz. Solvents were dried by standard methods and stored over Linde 4A molecular sieves prior to use. Organic extracts from reaction mixtures were dried by washing with brine and swirling with anhydrous sodium sulfate. All reactions were run under a dry nitrogen atmosphere.

Methyl 4-(*p*-Methoxyphenyl)butyrate (4). To a 500-mL round-bottomed flask was added 72.6 g (0.37 mol) of 4-(*p*-methoxyphenyl)butyric acid (**3**),[20] 60 mL of methanol, 200 mL of benzene, and 0.2 g of *p*-toluenesulfonic acid monohydrate. The resulting solution was magnetically stirred under reflux for 18 h. The solution was cooled, neutralized with solid sodium bicarbonate, and extracted with ether. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave a yellow-brown oil which was distilled at reduced pressure to give 72.2 g (93% yield) of water-white ester **4**: bp 111 °C (0.7 mm); IR (neat) 1737 cm^{-1} (ester >C=O); NMR (CCl_4) δ 1.65–2.64 (m, 6 H), 3.55 (s, 3 H), 3.68 (s, 3 H), and 6.59–7.13 ppm (symmetric m, 4 H); high resolution mass spectrum, calculated (*m/e*) for $C_{12}H_{16}O_3$, 208.1099; found, 208.1103.

2-Methyl-5-(*p*-methoxyphenyl)pentan-2-ol (5). A magnetically stirred solution of 50.0 g (0.24 mol) of ester **4** in 450 mL of anhydrous diethyl ether in a 2-L flame-dried round-bottomed flask was cooled to 0 °C. To the chilled solution was slowly added 352 mL of 1.5 M (0.53 mol) methyllithium in ether dropwise over a 1.5-h period. The reaction mixture was allowed to warm to room temperature and stirred 24 h. At this time excess methyllithium was decomposed by dropwise addition of water-saturated diethyl ether. Water (300 mL) was then added to dissolve the lithium salts and the mixture was extracted with ether. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave 50.0 g (100%) of tertiary alcohol **5**: IR (neat) 3435 (–OH), 1375, and 1365 cm^{-1} [$(CH_3)_2C<$]; NMR (CCl_4) δ 1.12 (s, 6 H), 1.37–166 (m, 4 H), 2.90 (broad s, 1 H), 2.34–2.65 (m, 2 H), 3.68 (s, 3 H), and 6.57–7.10 ppm (symmetric m, 4 H); high resolution mass spectrum, calculated (*m/e*) for $C_{13}H_{20}O_2$, 208.1463; found, 208.1468.

1,1-Dimethyl-7-methoxytetralin (6). A 1-L round-bottomed flask was charged with 49.5 g (0.24 mol) of tertiary alcohol **5**. To this was added 900 g of commercial polyphosphoric acid (Matheson Coleman and Bell, Inc.). The resultant mixture was mechanically stirred for 9 h at 50 °C during which time the color changed from clear to yellow to red. The mixture was cooled to room temperature and then poured into 800 mL of ice water. The aqueous layer was extracted four times with ether. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent at reduced pressure gave a brown oil which was distilled to give 42.2 g (94% yield) of dimethyltetralin **6** as a water-white oil: bp 85–87 °C (0.5 mm); IR (neat) 1381 and 1365 cm^{-1} [$(CH_3)_2C<$]; NMR (CCl_4) δ 1.23 (s, 6 H), 1.47–2.03 (m, 4 H), 2.44–2.80 (m, 2 H), 3.68 (s, 3 H), and 6.37–7.14 ppm (unsymmetrical m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{13}H_{18}O$, 190.1357; found, 190.1344.

4,4-Dimethyl-6-methoxy-1-tetralone (2). Into a 500-mL three-necked round-bottomed flask equipped with a mechanical stirrer and an addition funnel was placed 15.0 g (0.0788 mol) of dimethyltetralin **6** in 160 mL of glacial acetic acid. The solution was cooled to 10 °C. A solution of chromium trioxide, 23.7 g (0.237 mol) in 18 mL of water and 70 mL of acetic acid, was introduced into the addition funnel and two drops of this solution were added to the reaction mixture. At this time the reaction mixture was cooled to 0 °C and the chromium trioxide solution added dropwise over a 45-min period, maintaining the temperature at 0–5 °C. After addition was complete, the mixture was stirred at 0 °C for 24 h. The reaction was diluted with 200 mL of water and the mixture extracted five times with ether. The combined organic layers were washed with 5% sodium hydroxide until the aqueous washes were alkaline. The organic phase was washed with water until neutral and then dried. Removal of solvent gave a dark orange oil which was distilled to give 13.0 g (81% yield) of tetralone **2** as a pale yellow oil: bp 120–122 °C (0.1 mm); IR (neat) 1675 (conjugated >C=O), 1383 and 1362 cm^{-1} [$(CH_3)_2C<$]; NMR (CCl_4) δ 1.32 (s, 6 H), 1.74–2.09 (m, 2 H), 2.35–2.70 (m, 2 H), 3.78 (s, 3 H), and 6.54–7.94 ppm (m, 3 H); high resolution mass spectrum, calculated

for (*m/e*) $C_{13}H_{16}O_2$, 204.1150; found, 204.1146.

1-Methylene-4,4-dimethyl-6-methoxytetralin (7). To a flame-dried 50-mL three-necked round-bottom flask equipped with an efficient magnetic stirrer and a reflux condenser was added 1.26 g (0.030 mol) of sodium hydride as a 57% dispersion in mineral oil. This was washed three times with dry pentane, decanted, and then induced to react with 4 mL of dimethyl sulfoxide by heating to 70–75 °C until hydrogen evolution ceased (~40 min). The slurry was cooled to room temperature and 5 mL of dimethyl sulfoxide was added, followed by 12.18 g (0.030 mol) of methyltriphenylphosphonium iodide over a 15-min period. An additional 5 mL of dimethyl sulfoxide was added to make the mixture easier to stir. The mixture was stirred for 10 min, and then 3.06 g (0.015 mol) of tetralone **2** in 3 mL of dimethyl sulfoxide was added. The reaction mixture was stirred at 60–65 °C for 8 h. The material was then poured into a 125-mL Erlenmeyer flask containing 30 mL of ice water and 30 mL of pentane. The resulting mixture was vigorously stirred for 15 min, until the triphenylphosphine oxide precipitated. The mixture was filtered and the solid washed with pentane. The combined organic layers were washed with dimethyl sulfoxide–water (1:1) and water, and then dried. Removal of the solvent at reduced pressure gave 2.91 g (96% yield) of exocyclic olefin **7**: IR (neat) 1622 (ar >C=C<) and 875 cm^{-1} (>C=CH_2); NMR (CCl_4) δ 1.27 (s, 6 H), 1.54–1.84 (m, 2 H), 2.30–2.66 (m, 2 H), 3.71 (s, 3 H), 4.75 (m, 1 H), 5.21 (m, 1 H), and 6.45–7.53 ppm (m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{14}H_{18}O$, 202.1357; found, 202.1333.

Mixture of 9,9-Dimethyl-2-methoxy-6-benzosuberone (8) and 9,9-Dimethyl-2-methoxy-5-benzosuberone (1). (a) Using Filtered Cyanogen Azide Solution. To a 100-mL round-bottomed flask were added 2.95 g (0.0146 mol) of exocyclic olefin **7** and 30 mL of methanol–acetonitrile (1:1). To this was added 14.60 mL (0.0585 mol) of freshly prepared and filtered 4 M cyanogen azide solution[2] in acetonitrile. The solution was magnetically stirred for 72 h at ambient temperature during which time nitrogen evolution was noticeable. To the reaction mixture was added 15 mL of 6 M hydrochloric acid and the material was vigorously stirred at 50 °C for 4 h. This was cooled and extracted with ether. The ethereal extracts were washed with water until neutral and then dried. The dry organic phase was then percolated through a column of basic alumina capped with a layer of Celite to remove the explosive azide residues. Evaporation of the solvent gave 2.50 g of an orange oil which was then chromatographed. Elution with 50% dichloromethane–50% pentane from Florisil gave 1.89 g (59% yield) of ketone mixture **8** and **1**. Analysis of the crude product by NMR[4] prior to chromatography indicated a ratio of 92:8 **8**/**1**. Ketone **8** could be obtained in pure form by careful chromatography: IR (neat) 1711 cm^{-1} (>C=O); NMR (CCl_4) δ 1.37 (s, 6 H), 1.85–2.14 (m, 2 H), 2.28–2.55 (m, 2 H), 3.60–3.80 (m, 5 H including singlet at 3.69), and 6.38–6.98 ppm (m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{14}H_{18}O_2$, 218.1307; found, 218.1303.

(b) Using Unfiltered Cyanogen Azide Solution. In a manner exactly analogous to the one described above except that the cyanogen azide solution was not filtered prior to use, 0.404 g (0.002 mol) of exocyclic olefin **7** was subjected to ring expansion. Analysis by NMR[4] of the crude product after workup indicated a ratio of 65:35 **8**/**1**.

9,9-Dimethyl-2-methoxybenzosuberan (9). Amalgamated zinc was prepared by shaking 20.0 g of zinc powder, 2.0 g of mercuric chloride, 20 mL of water, and 1 mL of concentrated hydrochloric acid in a 100-mL round-bottomed flask for 10 min. The mixture was decanted. To the amalgamated zinc were added 1.39 g (0.00637 mol) of ketone mixture **8** and **1** and 60 mL of concentrated hydrochloric acid. After refluxing for 3 h, the mixture was cooled and extracted with ether. The organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave a tan oil which was chromatographed. Elution from neutral alumina with pentane gave 1.19 g (92% yield) of benzosuberan **9**: IR (neat) 1385 and 1360 cm^{-1} [$(CH_3)_2C$<]; NMR (CCl_4) δ 1.34 (s, 6 H), 1.50–1.95 (m, 6 H), 2.72–3.00 (m, 2 H), 3.70 (s, 3 H), and 6.35–7.00 ppm (m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{14}H_{20}O$, 204.1514; found, 204.1536.

Benzylic Oxidation of 9,9-Dimethyl-2-methoxybenzosuberan (9). (a) In a manner analogous to that described for preparation of compound **2**, 0.530 g (0.0026 mol) of benzosuberan **9** was oxidized at 0 °C for 24 h with chromium trioxide–acetic acid–water. Chromatography of the crude product on neutral alumina (50% dichloromethane–50% pentane) gave 0.035 g (6% yield) of benzosuberone **1**: IR (neat) 1673 cm^{-1} (conjugated >C=O); NMR (CCl_4) δ 1.38 (s, 6 H), 1.65–2.01 (m, 4 H), 2.35–2.79 (m, 2 H), 3.79 (s, 3 H), and 6.52–7.40 ppm (m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{14}H_{18}O_2$, 218.1307; found, 218.1313.

(b) The above experiment was repeated at room temperature for 28 h. Starting with 0.651 g (0.00319 mol) of benzosuberan **9**, the reaction yielded 0.073 g (10.5% yield) of desired benzosuberone **1** and only 0.117 g of unreacted starting material **9**.

Benzylic Oxidation of 2-Methoxybenzosuberan (10). (a) In a manner analogous to that described for preparation of compound **2**, 1.030 g (0.00585 mol) of benzosuberan **10** was oxidized at 0 °C for 24 h with chromium trioxide–acetic acid–water. The crude product was chromatographed on neutral alumina. Elution with 50% dichloromethane–50% pentane gave 0.133 g (12% yield) of crystalline benzosuberone **11**, which was identical with an authentic sample (Aldrich Chemical Co.): mp 60.5–61.0 °C; IR (CCl_4) 1673 cm^{-1}; NMR (CCl_4) 1.54–1.90 (m, 4 H), 2.53 (distorted t, 2 H), 2.79 (distorted t, 2 H), 3.70 (s, 3 H), and 6.46–7.70 ppm (m, 3 H).

(b) The above oxidation, using the same molar ratios, was performed on 0.995 g (0.00565 mol) of benzosuberan **10**. In this case the addition of the chromium trioxide solution was carried out between 25 and 30 °C and the reaction was allowed to go for 28 h at room temperature. Workup as before gave 0.791 g of gummy material which was chromatographed. Elution from neutral alumina with pentane gave 0.075 g of benzosuberan **10**. Further elution with 50% dichloromethane–50% pentane gave 0.676 g (63% conversion, 68% yield based on recovered starting material) of compound **11**.

9,9-Dimethyl-5-methylene-2-methoxybenzosuberan (15). In a manner analogous to that described for the preparation of compound **7** using the same molar ratios, 2.900 g (0.0133 mol) of benzosuberone **1** was reacted with the Wittig reagent derived from methyltriphenylphosphonium iodide to give 2.502 g (87% yield) of olefin **15**: IR (neat) 1625 (ar >C=C<) and 890 cm^{-1} (>C=CH_2); UV $\lambda_{max}^{95\%\ EtOH}$ 244 mμ (ϵ 8100); NMR (CCl_4) δ 1.23 (s, 6 H), 1.49–1.98 (m, 4 H), 2.05–2.44 (m, 2 H), 3.74 (s, 3 H), 4.85 (m, 2 H), and 6.32–7.07 ppm (m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{15}H_{20}O$, 216.1514; found, 216.1507.

5-Methylene-2-methoxybenzosuberan (17). In a manner analogous to that described for the preparation of compound **7** using the same molar ratios, 2.00 g (0.0105 mol) of benzosuberone **11** was reacted with the Wittig reagent derived from methyltriphenylphosphonium iodide. Workup as for exocyclic olefin **7** gave, after evaporation of the solvent, 1.88 g (95%) of olefin **17**: IR (neat) 1615 (ar –C=C) and 895 cm^{-1} (>C=CH_2); NMR (CCl_4) δ 1.55–2.86 (m, 8 H), 3.67 (s, 3 H), 4.93 (m, 2 H), and 6.41–7.16 ppm (m, 3 H); low resolution mass spectrum, parent peak (*m/e*) = 188.

Enol Ether 18. To a solution of 4.70 g (0.023 mol) of *gem*-dimethyl tetralone **2** in 75 mL of anhydrous methanol (in a 250-mL round-bottomed flask) were added 10 mL of methyl orthoformate and 0.1 g of *p*-toluenesulfonic acid. After the mixture was stirred at room temperature for 12 h, enough solid sodium methoxide was added to make the mixture slightly alkaline. The mixture was stirred 10 min. The methanol was removed at reduced pressure and the residue extracted with ether. The organic layers were combined and washed with water until neutral and then dried. Evaporation of the solvent gave 5.56 g of a thick red oil which was distilled to give 4.03 g (80% yield) of enol ether **18**: bp 113 °C (0.08 mm); IR (neat) 1648 cm^{-1} (>C=COR); NMR (CCl_4) δ 1.20 (s, 6 H), 2.14 (d, 2 H, J = 4.5 Hz), 3.55 (s, 3 H), 3.62 (s, 3 H), 4.54 (d, 1 H, J = 4.5 Hz), and 6.30–7.38 ppm (m, 3 H); high resolution mass spectrum, calculated (*m/e*) for $C_{14}H_{18}O_2$, 218.1307; found, 218.1313.

Dibromocyclopropane 19. Method A. To a 500 mL round-bottomed three-necked flask (equipped with a mechanical stirrer and an additional funnel) was introduced 4.01 g (0.0184 mol) of enol ether **18** in 90 mL of freshly distilled cyclohexane. Then 20 g of potassium *tert*-butoxide was added and the solution was chilled to 10 °C in an ice–water bath. To the cool solution was added 50 g of freshly distilled bromoform dropwise over a period of 2 h, maintaining the reaction temperature at or less than 20 °C. The mixture was allowed to warm to room temperature and stirred 12 h. After addition of 100 mL of water, the reaction mixture was extracted with dichloromethane. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave 7.25 g of a thick brown oil which was then chromatographed. Elution from Florisil with 20% dichloromethane–80% pentane gave 5.60 g (78% yield) of white crystalline dibromocyclopropane **19**. Other fractions rich in the desired product but containing varying amounts of impurities were combined and rechromatographed to give an additional 0.35 g of product (combined yield 83%). An analytical sample was recrystallized from pentane: mp 88.0–88.5 °C; IR (CCl_4) 1115 cm^{-1} (COC); NMR (CCl_4) δ 1.27 (s, 6 H), 1.46–2.43 (m, 3 H), 3.27 (s, 3 H), 3.69 (s, 3 H), and 6.41–7.38 ppm (m, 3 H). Anal. Calcd for $C_{15}H_{18}Br_2O_2$: C, 46.18; H, 4.65; Br, 40.96. Found: C, 45.99; H, 4.66; Br, 40.72.

Method B. In a 25-mL three-necked pear-shaped flask equipped

with a mechanical stirrer was placed 0.411 g (0.00189 mol) of enol ether 18 in 3 mL of freshly distilled bromoform and 0.020 g of Cetrimide. To this was added 3 mL of 33% aqueous sodium hydroxide dropwise over a 15-min period. The resulting two-phase mixture was vigorously stirred for 34 h at ambient temperature. Workup as in method A gave 0.715 g of a brown oil which on Florisil (elution with 20% dichloromethane–80% pentane) gave 0.507 g (69% yield) of crystalline material identical with that produced by method A.

Bromoenone 20. A solution of silver tetrafluoroborate was perpared along the lines of Birch and Keeton.[19] To 4.6 g of 37–40% aqueous hydrofluoroboric acid in a 10-mL Erlenmeyer flask equipped with a magnetic stirrer was slowly added 0.506 g (0.00218 mol) of silver oxide in small portions. The black silver oxide dissolved to give a clear pale gray solution, which was stirred an additional 10 min. At this time the silver tetrafluoroborate solution was slowly added to a 50-mL round-bottomed flask equipped with a magnetic stirrer and containing a solution of 0.850 g (0.00218 mol) of dibromocyclopropane 19 in 15 mL of ethanol. The mixture was stirred at reflux for 2 h. During the course of the reaction, silver bromide was formed as a granular precipitate. The solution was cooled to room temperature and transferred to a 125-mL Erlenmeyer flask and made alkaline (cautiously) with solid sodium carbonate. The solution was filtered to remove silver salts and the filtrate extracted with dichloromethane. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave 0.640 g of a brown oil which was chromatographed on Florisil. Elution with 20% dichloromethane–80% pentane gave 0.572 g (89% yield) of bromoenone **20** as a pale yellow oil: IR (neat) 1645 cm^{-1} (conjugated >C=O); NMR (CCl_4) δ 1.31 (s, 6 H), 2.41 (d, 2 H, J = 5.5 Hz), 3.71 (s, 3 H), 6.40–7.50 (m, 3 H), and 6.89 ppm (t, 1 H, J = 5.5 Hz); low resolution mass spectrum, parent peak: (m/e) = 204 (^{79}Br) and 206 (^{81}Br).

9,9-Dimethyl-2-methoxy-5-benzosuberone (1). A 25-mL round-bottomed flask was charged with 0.471 g (0.0016 mol) of bromoenone **20**. To this were added 0.150 g of 5% palladium on charcoal catalyst and 0.20 g of sodium carbonate, followed by 10 mL of benzene. The mixture was magnetically stirred as it was hydrogenated at room temperature and pressure for 8 h. At this time, the reaction mixture was filtered to remove the catalyst and excess sodium carbonate. The filtrate was evaporated at reduced pressure to give a yellow oil, which upon chromatography on Florisil (50% dichloromethane–50% pentane) gave 0.320 g (92% yield) of ketone **1**. This material was identical with that obtained from the direct oxidation of benzosuberan **2** with chromium trioxide in aqueous acetic acid.

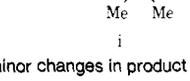
When 7.63 g (0.035 mol) of enol ether 18 was subjected to the sequence **18** → **19** → **20** → **1** using the same molar ratios and conditions, but not isolating the intermediate products, a yield of 6.33 g of ketone 1 was produced after column chromatography as above. This represents a yield of 83% from enol ether 18 (or 66% from tetralone **2**).

Acknowledgment. The authors wish to thank the Committee on Research, University of California, Davis, for partial support of this work.

Registry No.—**1**, 65275-82-3; **2**, 23203-51-2; **3**, 4521-28-2; **4**, 20637-08-5; **5**, 4586-90-7; **6**, 23203-50-1; **7**, 65275-83-4; **8**, 65275-77-6; **9**, 65275-78-7; **10**, 21336-18-5; **11**, 6500-65-8; **15**, 65275-79-8; **16**, 13587-99-0; **17**, 64746-51-6; **18**, 65275-80-1; **19**, 65354-45-2; **20**, 65275-81-2; methyllithium, 917-54-4; methyltriphenylphosphonium iodide, 2065-66-9; bromoform, 75-25-2.

References and Notes

(1) G. S. Krisna Rao, S. Dev, and P. C. Guna, *J. Indian Chem. Soc.*, **29**, 721 (1952); T. C. Joseph and S. Dev, *Tetrahedron*, **24**, 3861 (1968); R. Tabacchi, J. Garnero, and P. Buil, *Helv. Chim. Acta*, **57**, 849 (1974).
(2) J. McMurry and A. Coppolino, *J. Org. Chem.*, **38**, 2821 (1973).
(3) G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).
(4) Exocyclic olefin **8** isomerizes to endocyclic olefin i on contact with acid or on attempted distillation or chromatography.



i

(5) McMurry has noted minor changes in product distribution upon the addition of $AgBF_4$; see ref 2.
(6) These ratios were determined by integration of the NMR spectrum of the crude reaction product. Integration of the aromatic proton ortho to the carbonyl function in ketone **1** (δ = 7.29 ppm) relative to the remaining aromatic protons (no absorption past δ = 7.00 ppm) gave the reported ratios.
(7) Some conditions which failed were sodium dichromate–acetic acid in benzene both at room temperature and at reflux, and chromium trioxide in pyridine.
(8) Compound **10** was prepared from 6-methoxy-1-tetralone (Aldrich Chemical Co.) by a completely analogous route to that used for the preparation of compound **9** (see Scheme II). The yields of the individual steps were very similar in each case.
(9) Starting material disappeared after 36 h at room temperature but only a 52% yield of **11** was realized.
(10) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 285–291.
(11) R. Huisgen, *Angew. Chem.*, **69**, 341 (1957).
(12) D. P. Strike, T. Y. Jen, G. A. Hughes, G. H. Douglass, and H. Smith, *Steroids*, **8**, 309 (1966).
(13) (a) H. Rottendorf, S. Stenhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965); (b) J. D. Roberts and D. R. Davis, *J. Am. Chem. Soc.*, **84**, 2252 (1962).
(14) The splitting pattern of the two absorptions is also consistent with these assignments. H_a appears as a slightly broadened singlet while H_b shows much more splitting due to long-range coupling with the allylic methylene protons.[13b]
(15) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd ed, Wiley, New York, N.Y., 1974, p 218.
(16) For similar examples, see: Mme. Ramart-Lucas, *Bull. Soc. Chim. Fr., Ser. 5*, **1**, 719 (1934).
(17) M. Ephritikhine, J. Levisalles, and G. Teusch, *Bull. Soc. Chim. Fr.*, 4335 (1971).
(18) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972).
(19) A. Birch and R. Keeton, *J. Chem. Soc. C*, 109 (1968).
(20) F. Krollpfeiffer and W. Schäfer, *Chem. Ber.*, **56**, 630 (1923).

Synthesis and Novel Physical Properties of a Biphenoquinoquinocyclopropane

Larry A. Wendling and Robert West*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received September 23, 1977

The synthesis and physical properties of 1-(3,5-di-*tert*-butyl-4-hydroxy-4'-biphenylyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropene (**8**) are described. Upon oxidation with either PbO_2 or alkaline $K_3Fe(CN)_6$ **8** yields two major products. One of the products is tentatively identified as the fully quinoid system **4**, which displays a λ_{max} well into the near-infrared at 1300 nm. The other oxidation product is identified as the biradical **10**. The dianion of **8** can be electrochemically oxidized in an ESR cell to yield an anion radical identical with that obtained upon electrochemical reduction of **10**.

The quinocarbons (polyquinocycloalkanes) represent a class of radialenes in which each exocyclic double bond comprises either the ylidene linkage of a 4-oxo-2,5-cyclohexadien-1-ylidene moiety or a carbonyl group. Since the synthesis of the first quinocarbon, triquinocyclopropane **1**,[1] a number of other quinocarbons and related radialenes have been re-

0022-3263/78/1943-1573$01.00/0