1,2-H Shifts in Carbenes. The Benzonorbornenylidene System[1]

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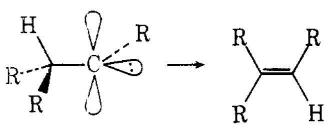
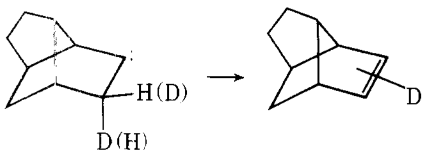
Four carbenes, 1-(*tert*-butyldimethylsiloxy)methyl-2-*exo*- and *endo*-deuterio-5,8-dimethoxybenzonorbornene-3-ylidene (**17b** and **17d**), and 1-(*tert*-butyldimethylsiloxy)methyl-3-*exo*- and -*endo*-deuterio-5,8-dimethoxybenzonorbornene-2-ylidene (**21b** and **21d**), were generated from the corresponding ketones via a thermal Bamford–Stevens route. The exo(x)-H to endo(n)-H migratory ratios were determined to be 13 (for **17**) and 18 (for **21**) at 190 °C. This leads to the activation energy differences $(E_a{}^n - E_a{}^x)^{190\,°C} = 2.4–2.7$ kcal/mol for the benzonorbornenylidene system.

Alkylcarbenes with an α-CH moiety undergo 1,2-H shifts to form olefins with such facility that it is often difficult to observe intermolecular reactions.[2] This reaction has been the subject of a number of theoretical investigations in recent years,[3] in which there has been general agreement that the migrating hydrogen proceeds from the conformation shown in **1**, where the empty p orbital and the C–H bond are essentially eclipsed. Calculations show that migration to the full (sp^2) orbital is a considerably higher energy process.[3d]



This question of stereoelectronic control of migration has been considered experimentally with conformationally mobile carbenes,[4] but ideally, a stereochemically well-defined, rigid carbene would be best to test the above theoretical predictions. Such a system was investigated recently by Nickon and his co-workers.[5,6] They found that, in the appropriately deuterium-labeled brexan-5-ylidene (**2**) systems generated from the corresponding sodium tosylhydrazone salts, an exo(x)-H to endo(n)-H migratory ratio of 138 could be derived.[5] Since the ethylene bridge in **2** tends to twist the methylene group α to the carbene center away from the conformation shown in **3** and approaching that in **4**, the preference for H_x migration over H_n presumably could be attributed to a stereoelectronic effect, in accord with theoretical calculations.[3] In order to arrive at this conclusion, however, it is necessary to assume that the H_x/H_n migratory ratio is close to unity in an undistorted bicyclo[2.2.1] system.[7]



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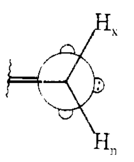

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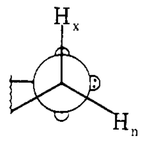

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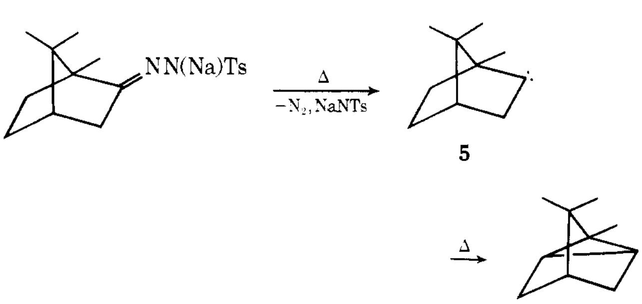
It is well known that in undistorted bicyclo[2.2.1] carbocations, the H_x/H_n migration ratio is very much larger than unity, although the reasons for this selectivity are not well understood.[8] Since there were no data available in the literature concerning migration tendencies in undistorted [2.2.1] carbenes, we undertook to investigate such a case to ascertain whether or not the above assumption was reasonable.

Results and Discussion

Synthesis. Our choice of substrate (**17** and **21**, Scheme I) was dictated by synthetic and analytical realities, along with a particular property of 2-bicyclo[2.2.1]carbenes. Thus it is well known that 2,3-H migration is not competitive with intramolecular cyclization in carbenes such as **5**.[9a] For this reason, it was necessary to use a substrate which would preclude such a reaction, and we chose a benzo group in the 5,6 position for this purpose.[9b] It was also necessary to have a "marker" on the molecule to identify the migration origin and terminus, and we placed this substituent on the bridgehead (1-) position when we found, after considerable preliminary work, that substituents on the benzo group did not impart sufficient differences to the two different positions in the olefin derived from the carbene to allow spectroscopic analysis. Finally, although the dioxygenated benzo group could have been avoided, the 5,8-dimethoxy substituents shifted the remaining aromatic protons far enough away from the olefinic protons in the ^{1}H NMR spectrum to facilitate spectroscopic analysis of the olefins **11b,c** derived from the carbenes **17** and **21**.



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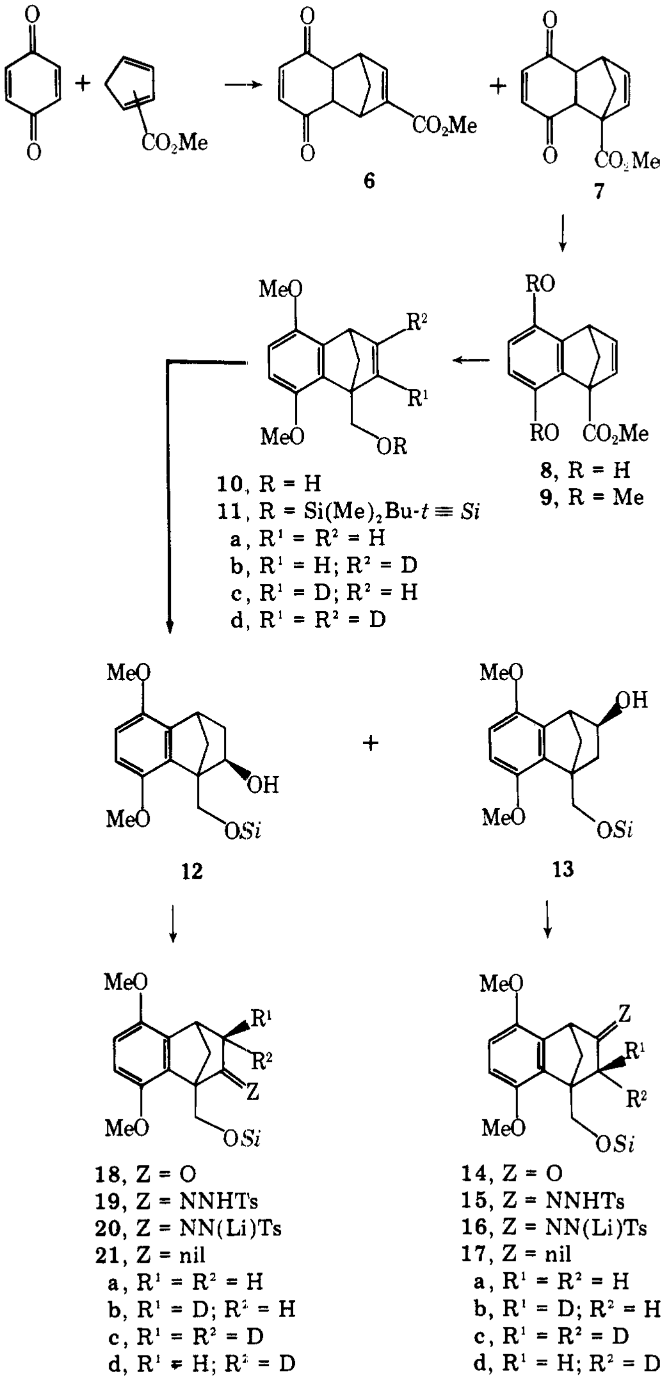
Reaction of carbomethoxycyclopentadiene (presumably a mixture of the 2 isomer and the 3 isomer) with *p*-benzoquinone gave a quantitative yield of a 3:1 mixture of Diels–Alder adducts **6** and **7**. Adduct **7** could be isolated in 30% yield by fractional crystallization from ether. Preferably, however, the mixture of **6** and **7** in dichloromethane was treated at room temperature with a small amount of concentrated hydrochloric acid and isomerized to a mixture of the corresponding hydroquinone derivatives, from which **8** could be isolated as a monohydrate (62%) by recrystallization from aqueous methanol. The quinol **8** was dimethylated to give **9** (87%) using potassium *tert*-butoxide and dimethyl sulfate in THF. Reduction of **9** with $LiAlH_4$ in ether gave alcohol **10** (92%), which was then protected using *tert*-butyldimethylsilyl chloride and imidazole in dry dimethylformamide[10] to give **11** in 86% yield. Treatment of **11** with disiamylborane in THF at −75 °C, followed by aqueous basic hydrogen peroxide, gave a mixture of regioisomers **12** and **13**, which could be separated by chromatography on alumina. The isolated yields of **12** and **13** using this procedure were 8 and 39%, whereas if borane in THF at 25 °C was used, the yields were 14 and 39%, respectively.

Scheme I



10, R = H
11, R = Si(Me)$_2$Bu-*t* ≡ *Si*
a, R^1 = R^2 = H
b, R^1 = H; R^2 = D
c, R^1 = D; R^2 = H
d, R^1 = R^2 = D

18, Z = O
19, Z = NNHTs
20, Z = NN(Li)Ts
21, Z = nil
a, R^1 = R^2 = H
b, R^1 = D; R^2 = H
c, R^1 = R^2 = D
d, R^1 = H; R^2 = D

14, Z = O
15, Z = NNHTs
16, Z = NN(Li)Ts
17, Z = nil
a, R^1 = R^2 = H
b, R^1 = D; R^2 = H
c, R^1 = R^2 = D
d, R^1 = H; R^2 = D

Consistent with the assigned structures, isomer **12** was much more mobile chromatographically, but much slower to oxidize under Oppenauer conditions than **13**. Thus oxidation of **13** using *p*-benzoquinone and tris(*tert*-butoxy)aluminum in refluxing benzene[11] required only 12 h for complete reaction (IR monitoring), whereas under the same conditions **12** required 72 h. Ketones **14a** and **18a** were isolated in 39 and 37% yields, respectively, after chromatography on alumina. The deuterated ketones **14b–d** and **18b–d** were then obtained by H–D exchange reactions using a slight modification of Tidwell's procedure.[12] Table I summarizes the deuterium content in these ketones.

Table I. Percentage (±2) Deuterium Content of Ketones 14b–d and 18b–d[a]

	14b	14c	14d	18b	18c	18d
d_0	0	0	8	6	1	5
d_1	93	0	81	93	5	83
d_2	7	100	11	1	94	12

[a] Registry no.: **14b**, 61149-99-3; **14c**, 61195-73-1; **14d**, 61247-13-0; **18b**, 61740-98-5; **18c**, 61740-99-6; **18d**, 61769-49-1.

The ^{1}H NMR spectra of **14a** and **18a** clearly establish their identities, particularly with respect to the location of the carbonyl group. Thus the methylene α to the carbonyl in **14a** gave an AB quartet centered at δ 2.09 ppm, J_{AB} = 17.0 Hz, ν_{AB} = 60.7 Hz, with the upfield doublet split further into doublets, J' = 4.0 Hz. This latter coupling is rationalized as W coupling[13] between the endo-2H and the proton syn to the aromatic ring on the bridging methylene group. This assigns the upfield (B) doublet of the AB quartet as due to the endo proton, and the deuterium exchange experiments confirm these assignments (vide infra). Ketone **14b** gave no resonance in the region assigned to the exo-H (A doublet of the AB quartet) and the upfield (B) doublet of doublets collapsed to a broadened doublet (H–D coupling) with a coupling constant of 4.0 Hz. The dideuterated material **14c**, of course, gave no absorption centered at δ 2.09, but **14d** showed the absence of resonance in the B portion of the AB quartet, and the A doublet collapsed to a broadened singlet. With **18a**, the methylene unit α to the carbonyl also gave an AB quartet centered at δ 2.19, J_{AB} = 17.0 Hz, ν_{AB} = 30.1 Hz, but in contrast to **14a**, *both* the A and B doublets were further split. The downfield (A) doublet was split cleanly into doublets, J' = 3.4 Hz, and the upfield doublets were split into multiplets which were not well resolved. These splittings may be rationalized on the basis that both exo- and endo-3H couple with the bridgehead (4) proton, but only the endo-3H undergoes W coupling[13] with the proton on the bridging methylene group. Here also, deuterium exchange experiments confirm these assignments. Thus, similar to **14b**, **18b** exhibited an ^{1}H NMR spectrum in which the downfield (A) resonance was not present, and the upfield doublet of multiplets collapsed to an ill-resolved narrow multiplet, while **18d** gave rise to the disappearance of the upfield (B) resonance and the collapse of the downfield (A) doublet of doublets to an ill-resolved doublet.

The Bamford–Stevens Thermolysis Route to Carbenes 17 and 21. The tosylhydrazones **15b,d** and **19b,d** were prepared in quantitative yields under neutral conditions from the corresponding ketones and *p*-tosylhydrazide in methanol solution at 60 °C for 1.3 h. The residue, obtained after concentration of the reaction mixture and evacuation at 70 °C (20 μ) for 2.5 h, was dissolved in THF and treated with *n*-butyllithium at −77 °C. The resulting solution was concentrated and evacuated at 70 °C (20 μ) for 1.5 h to give the lithium salts **16b,d** and **20b,d** as glasses. The salts were then decomposed in cyclohexane solution in a thick-walled glass tube by immersion in an oil both at 190 °C for 40 min. An unexceptional extractive workup followed by careful chromatography on alumina led to isolation of olefins **11a–d** in yields of 14–22%, as shown in Table II. Mass spectrometric analysis gave the distribution **11a**:**11b** + **11c**:**11d** (Table II), and indicated that little H–D exchange had occurred (compare deuterium content of ketones in Table I and olefins in Table II).

The exo/endo (x/n) migratory ratios required ^{1}H NMR analysis of the d_1 olefins (**11b,c**) in the olefinic region. The spectrum in this region consisted of a singlet at δ 6.49 ppm (aromatic protons) and an AB quartet centered at δ 6.74, with ν_{AB} = 11.1 Hz and J_{AB} = 5.2 Hz. The downfield (A) doublet was further split into doublets, J' = 3.0 Hz, and on this basis may be assigned to the proton at the 3 position, which is coupled to the bridgehead (4) proton.[14] With these assignments, analysis of the product olefins was possible. Thus, from the sequence **14b** → **15b** → **16b** → **11**, the H/D migratory ratio was determined to be ⅛ as follows. The ^{1}H NMR spectrum in the

Table II. Analysis of Olefins 11 Obtained from Thermolysis of 16b,d and 20b,d

Registry no.	Starting salt	% 11 isolated	% distribution^c **11a**	**11b**	**11c**	**11d**	Mig. ratio H/D	Mig. ratio H_x/H_n	$(E_a^n - E_a^x)^{190\ °C}$, kcal/mol
61848-85-9	**16b**	21^a	3	78	10	9	1/8	13	2.4
61490-24-2	**16d**	22^a	11	3.5	79.5	6	23/1		
61788-00-9	**20b**	14^b	3	12	81	4	1/7	18	2.7
61848-86-0	**20d**	20^b	6	80.3	1.7	12	47/1		

[a] Average of two runs. [b] Single determination. [c] The ratios **11a**:**11b** + **11c**:**11d** (±2%) were obtained mass spectrometrically. The ratios of **11b**:**11c** were obtained by ^1H NMR integration. Registry no.: **11a**, 61741-00-2; **11b**, 61195-72-0; **11c**, 61150-00-3; **11d**, 61827-39-2.

above-described olefinic region exhibited two absorptions, the major one at δ 6.68[5] (δ 6.74 − $\nu_{AB}/2$) as a singlet, and the minor absorption at δ 6.79[5] (δ 6.74 + $\nu_{AB}/2$) as a doublet (J' = 3.0 Hz, vide supra). These two absorptions are thus assigned to the D-migration (**11b**) and H-migration (**11c**) products, respectively. Multiple integrations (both electronic and planimetric) coupled with a small correction for the presence of 3% **11a** gave the ratio of **11b** to **11c** as 8:1 (Table II). Analogous procedures for the other three monodeuterated ketones generated the data in columns 3–7 in Table II.

The migratory ratios H_x/H_n can then be derived for the two regioisomeric carbenes **17a** and **21a** as follows. It is necessary to assume the same kinetic isotope effect (kie) for both exo and endo migration. Thus, for **17a**, the kie is obtained from the equations $y/x = 7.8$ and $yx = 23$, where x = the kie and y = the migratory ratio H_x/H_n. These calculations lead to a kie = 1.7 for **17** and 2.6 for **21**,[15] and to the migratory ratios shown in Table II. Assuming similar preexponential factors, these data lead to substantial activation energy differences for migration tendencies at 190 °C: $(E_a^n - E_a^x)^{190 °C} \sim 2.4$–2.7 kcal/mol.

Attempted Determination of Photolytic Migratory Aptitudes in 17 and 21. Numerous attempts at product analysis of the photolysis of **16** and **20** were unsuccessful. These salts were photolyzed using various combinations of suspensions in cyclohexane, solutions in dichloromethane or THF, with 254-nm light (Vycor), and a medium-pressure mercury lamp (Pyrex filter). Although one volatile product was formed during the photolysis as observed by GLC, this was not the olefin, as it had a longer retention time, and it disappeared during the course of the photolysis. Attempts to isolate and characterize this material failed. We did establish that olefin **11** was photolabile, but its rate of decomposition was such that it should have been observable if formed in the photolysis of **17** or **21** unless some species in the reaction mixture were sensitizing the photodecomposition of **11**.

Concluding Remarks. Similar to the bicyclo[2.2.1] carbocation situation, the origin of this propensity for H_x migration is at present not well understood.[17,18] It can be argued that the approximately tenfold greater tendency toward H_x migration in **2** than in **17** or **21** is due to a more favorable orbital alignment of H_x with the empty orbital on the carbene center in **2** than in **17** or **21**. We feel, however, that until it is understood why H_x migration is favored in the "unbiased" systems such as **17** and **21**, conclusions concerning orbital alignments drawn from migratory ratios derived from bi- and tricyclic systems are on tenuous grounds.

Experimental Section

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Infrared spectra (IR) were recorded on a Perkin-Elmer 237B grating spectrophotometer.

Proton magnetic resonance spectra (^1H NMR) were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instruments. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are reported in hertz. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Mass spectra were determined on a CEC-21-100 high-resolution instrument or a Du Pont 21-491 instrument.

Gas chromatographic analyses were performed on either a Varian-Aerograph 2720 (thermal conductivity detector) or 2740 (flame ionization detector) instrument using either 5% or 20% SE-30 on Gas Chrom Q, packed in stainless steel columns (6 ft by 0.188 in. or 6 ft by 0.125 in.). Peak area measurements were obtained with the aid of a Vidar 6300 digital integrator.

1-Carbomethoxy-*endo*-tricyclo[6.2.1.^{2,7}]undeca-4,9-diene-3,6-dione (7). Carbomethoxycyclopentadiene dimer (36.0 g, 0.145 mol) was cleaved distillatively (dry ice trap) to give the monomer diene esters (18.0 g, 50%), bp 100–120 °C (25 mm). This was dissolved in dichloromethane (40 mL) at −75 °C and added in one portion to *p*-benzoquinone (16.7 g, 0.155 mol) suspended in benzene (80 mL) at 25 °C. The solution was stirred overnight, the solvent was evaporated, and excess benzoquinone was removed under high vacuum (40 °C, 10 μ, 2.5 h) to afford a 3:1 mixture of the isomeric adducts **6** and **7**, respectively (^1H NMR **6**, q_{AB} centered at δ 6.23 vs. **7**, br d, δ 6.97). Fractional crystallization from ether afforded isomerically pure **6** as pale yellow needles (10.1 g, 30%): mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 6.61 (s, 2 H), 6.20 (q_{AB}, ν_{AB} = 9.8 Hz, J_{AB} = 5.5 Hz, upfield (B) doublet further split, J' = 3.0 Hz, 2 H), 3.83 (s, 3 H), 3.60 (m, 3 H), 1.81 (m, 2 H): IR ($CHCl_3$) 1735, 1670, 1605 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.18; H, 5.33.

1-Carbomethoxy-5,8-dihydroxybenzonorbornadiene Monohydrate (8). Concentrated hydrochloric acid (0.3 mL) was added with vigorous stirring to the mixture of quinone adducts **6** and **7** (15.5 g, 66.8 mmol) in dichloromethane (25 mL). After 2 h, the solvent was evaporated to leave a tan solid (15.5 g, 100%). Recrystallization ($MeOH–H_2O$, 1:2 v/v) gave isomerically pure **8** H_2O as white crystals (10.3 g, 62%): mp 99–103 °C; ^1H NMR (acetone-d_6) δ 8.6–8.25 (br s, 1 H), 8.1–7.45 (br s, 1 H), 6.84 (m, 2 H), 6.36 (d, J = 1.5 Hz, 2 H), 4.18 (m, 1 H), 3.82 (s, 3 H), 3.46 (br s, 2 H), 2.41 (d, J = 1 Hz, 2 H); IR (KBr) 3315, 1715 m^{-1}.

Anal. Calcd for $C_{13}H_{12}O_4 \cdot H_2O$: C, 62.39; H, 5.64. Found: C, 62.56; H, 5.55.

1-Carbomethoxy-5,8-dimethoxybenzonorbornadiene (9). The quinol ester **8** (10.75 g, 139 mmol) and dimethyl sulfate (52.5 g, 417 mmol) in dry THF at 0 °C under nitrogen were treated with three portions of potassium *tert*-butoxide (3 × 5.19 g, 139 mmol) at 1-h intervals. The mixture was stirred overnight and filtered and the filtrate was dried ($MgSO_4$), and then concentrated to give a brown solid. Recrystallization (hexane) gave white needles (10.5 g, 87%), mp 77–80 °C. An analytical sample was prepared by thermal gradient sublimation (70 °C, 10 μ) to give white needles: mp 79–80 °C; ^1H NMR ($CDCl_3$) δ 6.92 (q_{AB}, ν_{AB} = 14 Hz, J_{AB} = 5.5 Hz, upfield (B) doublet further split, J' = 3 Hz, 2 H), 6.51 (s, 2 H), 4.20 (m, 1 H), 3.83 (s, 3 H), 3.75 (s, 3 H), 3.70 (s, 3 H), 2.51 (q_{AB}, ν_{AB} = 11 Hz, J_{AB} = 7 Hz, upfield (B) doublet further split, J' = 1.5 Hz, 2 H); IR ($CHCl_3$) 1730 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.31; H, 6.12.

1-Hydroxymethyl-5,8-dimethoxybenzonorbornadiene (10). The ester **9** (9.00 g, 34.6 mmol) in dry ether (125 mL) was added dropwise to $LiAlH_4$ (1.14 g, 30.0 mmol) in ether (200 mL) at 0 °C and then stirred overnight at 25 °C. The cooled (0 °C) mixture was treated successively with water (1.14 mL), 3 N aqueous sodium hydroxide (1.14 mL), and water (3.42 mL). After vigorous stirring (1 h) the mixture was filtered, the filter cake washed with ether, and the combined organic portions dried ($MgSO_4$) and concentrated to give a viscous, tan oil (8.10 g, 92%). The oil solidified upon standing and recrystallization (hexane) afforded white needles: mp 68–69.5 °C; ^1H NMR ($CDCl_3$) δ 6.82 (m, 2 H), 6.53 (s, 2 H), 4.13 (m, 4 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 2.17 (m, 2 H); IR ($CHCl_3$) 3485 cm^{-1}.

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.39; H, 6.67.

1-(*tert*-Butyldimethylsiloxy)methyl-5,8-dimethoxybenzonorbornadiene (11a). To a solution of alcohol **10a** (6.70 g, 28.9 mmol) and imidazole (2.26 g, 33.2 mml) in dry dimethylformamide (100 mL) at 25 °C was added *tert*-butyldimethylsilyl chloride[10] (5.00 g, 33.2 mmol) and the mixture stirred for 2 h. After the addition of water (150 mL) the cloudy mixture was extracted with pentane (4 × 100 mL). The combined pentane extracts were then dried ($MgSO_4$) and concentrated to give a white solid (8.60 g, 86%). An analytical sample was prepared by thermal gradient sublimation (70 °C, 10 μ) to give white needles: mp 92.5–93.5 °C; ^1H NMR ($CDCl_3$) δ 6.74 (q_{AB}, ν_{AB} = 11.1 Hz, J_{AB} = 5.2 Hz, downfield (A) doublet further split, J' = 3.0 Hz, 2 H), 6.49 (s, 2 H), 4.49 (q_{AB}, ν_{AB} = 31 Hz, J_{AB} = 11 Hz, 2 H), 4.12 (m, 1 H), 3.77 (s, 3 H), 3.72 (s, 3 H), 2.27 (q_{AB}, ν_{AB} = 30 Hz, J_{AB} = 7 Hz, both doublets (A and B) further split, J' = 2 Hz, 2 H), 0.91 (s, 9 H), 0.125 (s, 3 H), 0.115 (s, 3 H); MS (70 eV) *m/e* (rel intensity) 346 (7), 289 (100), 274 (90), 259 (31).

Anal. Calcd for $C_{20}H_{30}O_3Si$: C, 69.32; H, 8.73. Found: C, 69.35; H, 8.70.

1-(*tert*-Butyldimethylsiloxy)methyl-5,8-dimethoxybenzonorbornene-*exo*-3-ol (13) and 1-(*tert*-Butyldimethylsiloxy)methyl-5,8-dimethoxybenzonorbornen-*exo*-2-ol (12). A. Hydroboration of 11 with Disiamylborane. A 1.3 M solution of BH_3·THF (102 mL, 133 mmol) was added to 2-methyl-2-butene (21.0 g, 300 mmol) in dry THF (150 mL) at 0 °C. The mixture was stirred at 25 °C for 2.5 h, then cooled to −75 °C. To this solution was added 11 (13.2 g, 38.2 mmol) in THF (75 mL). The reaction mixture was warmed slowly and stirred overnight and then excess borane was decomposed by the addition of ice chips after cooling (0 °C). When the foaming had subsided 3 N aqueous sodium hydroxide (70 mL) was added followed by 30% aqueous hydrogen peroxide (70 mL) and the mixture was stirred for 2 h. The organic layer was separated, the THF was removed, and the aqueous layer was extracted with ether (2 × 100 mL). The combined organic portions were washed with 1 M hydrochloric acid, 5% aqueous sodium bicarbonate, and brine and dried ($MgSO_4$). The solvent was evaporated to give an oil (14.4 g) which contained a mixture of the isomers 12 and 13.

Chromatography (alumina, CH_2Cl_2) afforded separation of the two isomers. The faster moving component, 12, was obtained as a mobile, colorless oil (1.10 g, 8%). An analytical sample was prepared by distillation (Kugelrohr, 105 °C, 20 μ): ^1H NMR ($CDCl_3$) δ 6.59 (s, 2 H), 4.65 (q_{AB}, ν_{AB} = 42.5 Hz, J_{AB} = 11 Hz, 2 H), 4.52 (br s, 1 H), 4.00 (m, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.50 (m, 1 H), 2.01 (br q_{AB}, ν_{AB} = 42 Hz, J_{AB} = 9 Hz, 2 H), 1.78 (m, 2 H), 0.92 (s, 9 H), 0.14 (s, 3 H), 0.12 (s, 3 H); IR ($CHCl_3$) 3500 cm^{-1}.

Anal. Calcd for $C_{20}H_{32}O_4Si$: C, 65.89; H, 8.85. Found: C, 65.94; H, 8.67.

The slower moving isomer, 13, was a viscous, colorless oil (5.42 g, 39%). An analytical sample was prepared by distillation (Kugelrohr, 105 °C, 20 μ): ^1H NMR ($CDCl_3$) δ 6.60 (s, 2 H), 4.30 (br s, 2 H), 4.01 (m, 1 H), 3.77 (s, 3 H), 3.72 (s, 3 H), 3.42 (m, 1 H), 1.97 (complex m, 5 H), 0.92 (s, 9 H), 0.09 (s, 6 H); IR ($CHCl_3$) 3580, 3400 cm^{-1}.

Anal. Calcd for $C_{20}H_{32}O_4Si$: C, 65.89; H, 8.85. Found: C, 65.66; H, 8.83.

The intermediate chromatography fractions contained a mixture of the two isomers (1.35 g).

B. Hydroboration of 11 with Borane. A 1.3 M solution of BH_3·THF (10 mL, 13 mmol) was added to the olefin 11 (2.97 g, 8.58 mmol) in dry THF (50 mL) at 0 °C. The solution was allowed to warm to room temperature and then to stir for 4 h. Workup as above gave an oil (2.86 g) consisting of a mixture of 12 and 13, which were isolated in yields of 14 and 39%, respectively, by chromatography as described above.

1-(*tert*-Butyldimethylsiloxy)methyl-5,8-dimethoxybenzonorbornen-3-one (14a). A mixture of alcohol 13 (5.02 g, 13.74 mmol), *p*-benzoquinone (2.00 g, 18.5 mmol), and tris(*tert*-butoxy)aluminum (7.35 g, 29.9 mmol) in benzene (200 mL) was heated at reflux for 12 h. The cooled mixture was stirred with 10% aqueous sulfuric acid (510 mL) for 1 h. The organic layer was separated, washed with 10% aqueous sulfuric acid (2 × 100 mL), 10% aqueous sodium hydroxide (until the aqueous washes remained colorless), water, and brine, dried ($MgSO_4$), and concentrated to give a yellow solid (3.88 g). Chromatography (alumina, pentane/CH_2Cl_2, 7:3 v/v) gave a white solid (1.92 g, 39%), mp 117–119 °C. An analytical sample was obtained from thermal gradient sublimation (105 °C, 10 μ) as fine, white crystals: mp 118–119 °C; ^1H NMR ($CDCl_3$) δ 6.68 (s, 2 H), 4.36 (q_{AB}, ν_{AB} = 28.0 Hz, J_{AB} = 11.0 Hz, 2 H), 3.85 (m, 1 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 2.09 (q_{AB}, ν_{AB} = 60.7 Hz, J_{AB} = 17.0 Hz, upfield (B) doublet split further into doublets, J' = 4.0 Hz, 2 H), 2.30 (m, 2 H), 0.91 (s, 9 H), 0.10 (s, 6 H); IR ($CHCl_3$) 1735 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 362 (4), 305 (100), 262 (15), 248 (22), 189 (28).

Anal. Calcd for $C_{20}H_{30}O_4Si$: C, 66.26; H, 8.34. Found: C, 66.19; H, 8.32.

1-(*tert*-Butyldimethylsiloxy)methyl-5,8-dimethoxybenzonorbornen-2-one (18a). A mixture of alcohol **12** (1.02 g, 280 mmol), *p*-benzoquinone (0.417 g, 3.86 mmol), and tris(*tert*-butoxy)aluminum (1.55 g, 6.30 mmol) in benzene (40 mL) was heated at reflux for 72 h. Workup as above and chromatography (alumina, pentane/CH_2Cl_2, 2:1 v/v) gave **18a** as a white solid (375 mg, 37%). An analytical sample was prepared by thermal gradient sublimation (105 °C, 20 μ) to give white crystals: mp 98–99 °C; ^1H NMR ($CDCl_3$) δ 6.62 (q_{AB}, ν_{AB} = 8 Hz, J_{AB} = 9 Hz, 2 H), 4.41 (q_{AB}, ν_{AB} = 43 Hz, J_{AB} = 11 Hz, 2 H), 3.78 (s) + 3.76 (m) + 3.69 (s) (total 7 H), 2.37 (m, 2 H), 2.19 (q_{AB}, ν_{AB} = 30.1 Hz, J_{AB} = 17.0 Hz, downfield (A) doublet split further into doublets, J' = 3.4 Hz, upfield (B) doublet split into poorly resolved multiplets, 2 H), 0.88 (s, 9 H), 0.09 (s, 6 H); IR ($CHCl_3$) 1745 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 362 (3), 305 (100), 262 (12), 248 (13), 189 (15).

Anal. Calcd for $C_{20}H_{30}O_4Si$: C, 66.26; H, 8.34. Found: C, 66.50; H, 8.54.

Preparations of the Deuterio Derivatives of 14. A. 1-(*tert*-Butyldimethylsiloxy)methyl-2-*exo*-deuterio-5,8-dimethoxybenzonorbornen-3-one (14b). To ketone **14a** (937 mg, 2.59 mmol) in dry dioxane (50 mL) was added potassium *tert*-butoxide (415 mg, 3.17 mmol) dissolved in deuterium oxide (25 mL). The mixture was heated at 60 °C for 1.25 h and quenched with a mixture of saturated aqueous ammonium chloride (50 mL) and dichloromethane (70 mL). The layers were separated and the aqueous portion extracted with pentane (5 × 40 mL). The combined organic portions were washed with brine and dried ($MgSO_4$), and the solvent was removed to afford **14b** (909 mg, 95%) as a white solid.

Mass spectral analysis of the base peak region (*m/e* 305–309) gave the ratios of $d_0{:}d_1{:}d_2$ = 0:93:7 (±2). The ^1H NMR analyses of **14b**, **14c**, and **14d** are described in the body of the paper.

B. 1-(*tert*-Butyldimethylsiloxy)methyl-2,2-dideuterio-5,8-dimethoxybenzonorbornen-3-one (14c). To ketone **14a** (2.32 g, 6.41 mmol) in dioxane (120 mL) was added potassium *tert*-butoxide (0.90 g, 8.0 mmol) dissolved in deuterium oxide (60 mL). The mixture was stirred at 60 °C for 96 h and worked up as above. Some of the silyl protecting group had been removed during the long reaction period, so the mixture was resilylated in the usual way to give **14c** (2.20 g, 95%).

Mass spectral analysis gave $d_0{:}d_1{:}d_2$ = 0:0:100 (±2).

C. 1-(*tert*-Butyldimethylsiloxy)methyl-2-*endo*-deuterio-5,8-dimethoxybenzonorbornen-3-one (14d). Treatment of **14c** (2.20 g, 6.04 mmol) in dioxane (120 mL) with potassium *tert*-butoxide (0.90 g, 8.0 mmol) dissolved in water (60 mL) at 60 °C for 2.6 h followed by workup and reprotection of the desilyated material (~10%) gave **14d** (2.14 g, 97%).

Mass spectral analysis gave $d_0{:}d_1{:}d_2$ = 8:81:11 (±2).

Preparations of the Deuterio Derivatives of 18. Compounds **18b**, **18c**, and **18d** were prepared by procedures parallel to those for compounds **14b–d**. The deuterium contents of the materials are given in Table I.

Preparation of the Tosylhydrazone Derivatives and Their Lithium Salts. The following is a representative procedure. The ketone **14b** (1.84 g, 5.07 mmol) was dissolved in absolute methanol (180 mL) at 60 °C, *p*-toluenesulfonylhydrazide (0.99 g, 5.32 mmol) was added, and the mixture was stirred at 60 °C for 1.3 h. The solution was concentrated and the residue warmed under vacuum (70 °C, 20 μ, 2.5 h). The resulting solid was dissolved in dry THF (50 mL) and treated at −75 °C under nitrogen with a 1.34 M hexane solution of *n*-butyllithium (4.73 mL, 6.34 mmol). The resulting solution was warmed slowly to 25 °C and concentrated, and the residue was heated under vacuum (70 °C, 20 μ, 1.5 h) to give a glass **16b** (2.46 g).

Pyrolysis of the Tosylhydrazone Salts 16 and 20. A representative procedure is as follows. The salt **16b** (827 mg, 1.77 mmol) was suspended in dry cyclohexane (~20 mL) in a Fisher-Porter combustion tube vessel with an aluminum and Teflon sealing disk and standard pipe coupling. The tube was heated in an oil bath (190 ± 2 °C) for 40 min. After cooling, the reaction mixture was partitioned between water (20 mL) and dichloromethane (50 mL). The organic layer was washed with brine, dried ($MgSO_4$), and concentrated to give a yellow solid (460 mg). Chromatography (alumina, pentane/CH_2Cl_2, 9:1 v/v) gave the olefin **11** (22%) (see Table II).

Mass spectral analysis (*m/e* 289–294 cluster) determined the ratio **11a**:**11b** + **11c**:**11d** (Table II). The ^1H NMR analyses of the olefinic mixtures were carried out as described in the body of the paper.

Photolyses of 1-(*tert*-Butyldimethylsiloxy)methyl-5,8-dimethoxybenzonorbornadiene (11). A. The olefin **11** (12.9 mg, 0.037 mmol) in degassed dichloromethane (1 mL) with octadecane (5.5 mg, 0.022 mmol) as an internal standard was photolyzed in a Pyrex tube with a Hanovia 450-W medium-pressure mercury arc lamp contained in an ice-water-cooled Pyrex well. The course of the reaction was monitored by flame ionization GLC (6 ft × 0.125 in., SE-30 5% on Gas Chrom Q). The concentration of **11** decreased (only 52% remaining after 2 h 40 min and <23% after 5 h) and a new peak arose having a longer retention time than that of the olefin (**11**). After 3.5 h the new peak began to decrease and was absent after 5.5 h.

B. The olefin **11** (12.5 mg, 0.036 mmol) in degassed cyclohexane (1 mL) in a Vycor tube was irradiated in a Rayonet photochemical reactor (254 nm) and the reaction was followed by GLC as above. Similar results to the first photolysis were noted as the olefin concentration decreased, although more rapidly (<50% olefin remained after 1.5 h), and the new peak of longer retention time arose and then rapidly decreased. After 2.5 h both the olefin peak and the unknown peak were absent from the GLC trace.

Attempts to Isolate the Unknown Compound Formed in the Photolysis of 11. A solution of **11** (80 mg, 0.23 mmol) in degassed dichloromethane (5 mL) was irradiated (254 nm) for 2.4 h in a Pyrex tube. After removal of the solvent the residue was chromatographed ("dry column", Al_2O_3/CH_2Cl_2). Three bands showing ultraviolet activity were removed but none contained the unknown material (by GLC). The remaining Al_2O_3 sections were washed with dichloromethane. The combined washes were concentrated to give an oil (~4 mg) which gave a major GLC peak at the same retention time as the unknown compound. This material was analyzed by GC/MS: major peaks at *m/e* 346, 289, 274, 259, 215, and 57. This spectrum was very similar to that of **11**, except that *m/e* 57 was reduced in intensity, and *m/e* 215 was much increased relative to those in the spectrum of **11**. No further attempts were made to isolate and identify this unknown material.

Photolysis of the Tosylhydrazone Salt 16a. A. A suspension of **16a** (121 mg, 0.26 mmol) in degassed cyclohexane (2 mL) was irradiated (254 nm) in a Vycor tube. No olefin **11** formation was detectable (GLC and TLC) and a new, longer retention peak (the same unknown GLC peak seen in photolysis of **11** above) arose slightly but disappeared upon further irradiation (~3 h).

B. A degassed cyclohexane (2 mL) suspension of **16a** (100 mg, 0.21 mmol) in a Pyrex tube was irradiated with a Hanovia 450-W medium-pressure Hg arc lamp. Results essentially identical with the above photolysis were obtained. No olefin **11** formation was detectable (GLC and TLC).

C. Further experiments using homogeneous solutions (CH_2Cl_2 and THF) of **16a** resulted in similar negative results.

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(15) The latter number is considerably less reliable, since it was obtained from single determinations due to unavailability of sufficient amounts of **18b** and **18d.** If the difference is real we have no rationalization for it. The kie's >1 are in accord with Nickon's observations for **2**,[4] but differ from the results of Kirmse,[16] who found kie = 1.00 for the *thermal* generation of 2-H and 2-D-1-propylidene.

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