Registry No.—A, 4209-13-6; 1, 6214-32-0.

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Hydrogen Migration in 2-Carbena-6,6-dimethylnorbornane[1]

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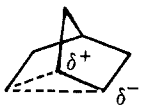
A study of the dry salt pyrolysis and the photolysis of the lithium salts of the tosylhydrazone of 6,6-dimethylnorbornan-2-one, *exo*-3-deuterio-6,6-dimethylnorbornan-2-one, and *endo*-3-deuterio-6,6-dimethylnorbornan-2-one revealed a preference for exo-C-3 → exo-C-2 over endo-C-3 → endo-C-2 hydride migration of approximately 20:1. This stereoselectivity is interpreted in terms of torsional interactions in the hydride migration transition state of a classical singlet carbene.

Although studies of the chemistry of the 2-norbornyl carbonium ion have absorbed the attention of many chemists over the past 25-year period,[3] and substantial effort has been expended in investigations of the nature of the related radical intermediate,[4] much less is known concerning the analogous carbanion[5] and carbene intermediates.[6] A consideration of this history suggests that characterization of 2-carbenanorbornane might be of considerable interest, since, in the singlet state, delocalization involving the empty p orbital at C-2 and the C-1–C-6 σ bond is possible (**1**).



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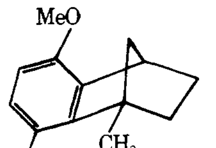
Since most alicyclic carbene intermediates react by way of intramolecular rather than intermolecular pathways,[7] characterization of a 2-carbenanorbornane intermediate would appear to require the analysis of an insertion or hydrogen migration reaction. The nature of the 2-norbornyl carbonium ion has been revealed to some degree through studies of the stereospecificity of 3,2-hydride shifts. Investigations by Collins[8] and Berson[9] have shown that exo-C-3 to exo-C-2 hydride migration is preferred over endo-C-3 to endo-C-2 migration ($k_{\text{exo-exo}}$:$k_{\text{endo-endo}} > 100$). Since 1,2 hydrogen shifts are common intramolecular reaction pathways for bivalent carbon intermediates,[7] it appeared to us that a study of the stereochemistry of the C-3–C-2 hydride shift in 2-carbenanorbornane would be an excellent approach to an understanding of the chemistry of this intermediate. Unfortunately, 2-carbenanorbornane reacts predominantly via C-6 insertion with C-3–C-2 hydrogen migration as a barely detectable component of the reaction (nortricyclene–norbornene = 99.5:0.5).[6a] This difficulty was circumvented in a recent study by Kyba and Hudson,[10] who studied the benzo-2-carbenanorborene intermediate **2**, whereas Nickon and co-workers[11] have investigated 2-carbenanorbornane species **3**, which possesses a built-in bias favoring exo-C-3 hydrogen migration, since the additional bridge twists the exo-C-3 hydrogen into coplanarity with the empty p orbital of the adjacent singlet carbene center. Our approach is to consider 2-carbena-6,6-dimethylnorbornane (**12**), since much of the simplicity and symmetry of the parent system is preserved and γ C–H insertion is blocked, C–C insertion being a rarely observed process.[12]



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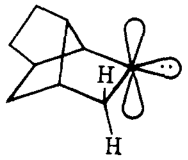

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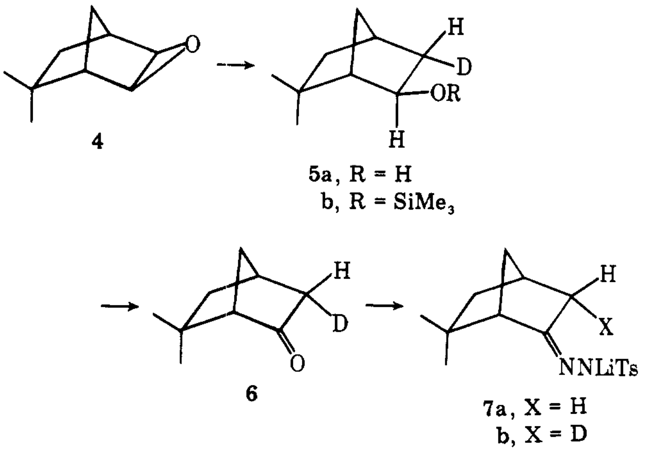
The required *endo*- and *exo*-deuterated tosylhydrazone lithium salts (**7b** and **10**) were prepared starting with 5,5-dimethylnorbornene epoxide (**4**)[13] and 6,6-dimethylnorcamphor (**8**).[13] Epoxide **4** with lithium aluminum deuteride treatment followed by chromic acid oxidation produces *endo*-3-deuterio-**6**. Treatment of **6** with $TsNHNH_2/H^+$ yields tosylhydrazone, which is converted to lithium salt with an equivalent of methyllithium. Ketone **8** was converted to *exo*-deuteriotosylhydrazone salt by treatment with CH_3ONa/CH_3OD, conversion to tosylhydrazone and subsequently to lithium salt **10** as in the endo case.

Table I. Results of Decompositions of Tosylhydrazone Salts 10 and 7b

			Mass spectra of 11			NMR integration of 4	
Run	Salt	Type	d_0	d_1	d_2	C-2	C-3
1	**10**	Pyr.[a]	17.9 ± 0.9[c]	78.3 ± 2.1	3.8 ± 1.5	0.938 ± 0.097	0.222 ± 0.090
2	**10**	Pyr.	9.4 ± 0.3	82.2 ± 1.1	8.4 ± 0.7	0.844 ± 0.028	0.149 ± 0.060
3	**7b**	Pyr.	3.4 ± 0.4	96.6 ± 0.4	0.0	0.097 ± 0.011	0.937 ± 0.077
4	**10**	Phot.[b]	43.4 ± 0.5	56.6 ± 0.5	<0.5	0.979 ± 0.071	0.456 ± 0.046
5	**7b**	Phot.	5.2 ± 0.2	94.8 ± 0.2	0.0	0.104 ± 0.030	0.947 ± 0.039

[a] Dry salt pyrolysis. [b] Photolysis in THF. [c] One standard deviation.

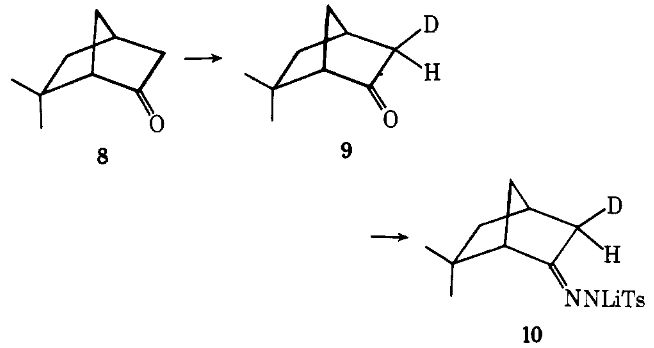


4

5a, R = H
b, R = SiMe$_3$

6

7a, X = H
b, X = D



8

9

10

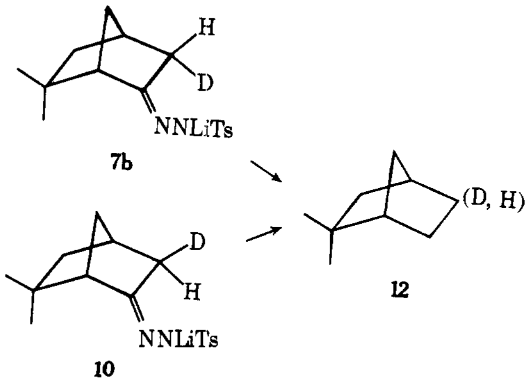
Table II. Product Composition in the Decomposition of Tosylhydrazone Salts 7b and 10

Tosylhydrazone	Type	11b	11c
10	Dry salt	4.6 ± 1.2%[a]	95.4 ± 2.0%
10	Dry salt	5.8 ± 1.2	94.2 ± 2.0
7b	Dry salt	93.5 ± 1.6	6.5 ± 1.2
10	Photolysis	3.9 ± 1.4	96.1 ± 2.7
7b	Photolysis	94.5 ± 1.3	5.5 ± 0.4

[a] Standard deviation.

Analysis of the stereochemistry of hydride migration in the labeled 2-carbena-6,6-dimethylnorbornane species generated from tosylhydrazones **7b** and **10** will not be hindered by the presence of undeuterated tosylhydrazone (corrected for in the NMR analysis) nor by dideuterated tosylhydrazone (undetected in the NMR analysis). Only epimerization in the preparation of **7b** and **10** would present an analytical problem. A complication of this nature was tested for by conversion of **5a** to the trimethylsilyl derivative **5b** (97.8 ± 0.1% d_1) and then transforming **5a** → **6** → **7b**. Lithium salt **7b** was reconverted to tosylhydrazone (HOAc) and then to **6** (97.8 ± 0.1% d_1), using the NBS treatment[14] previously determined not to affect C_α.[15] Since epimerization would presumably occur through enolate formation and since deuterated enolate would re-form **6** much more rapidly than epimer **9**, the rate of enolate formation would be considerably greater than the rate of epimerization. Allowing for an isotope effect of perhaps 4–7 for exo hydrogen abstraction, epimerization that occurs should be accompanied by deuterium loss.[5l] Since no deuterium loss occurs, there is no epimerization. In the case of *exo*-3-deuterio-**9**, *exo*-3-deuterium loss should predominate over *endo*-3-hydrogen abstraction[5l,m,n] and, as a consequence, any epimerization which might occur should be accompanied by a large amount of deuterium loss. Ketone **9** was analyzed by NMR, with the aid of an Eu(fod)$_3$ chemical shift study, before conversion to tosylhydrazone (7.0% d_0) and after reconversion to ketone (NBS) from tosylhydrazone (6.0% d_0). A similar experiment which included lithium salt **10** in the cycle revealed no deuterium loss (less than 2%). Even though the preparation of the desired carbene precursors **7** and **10** appears to be free of complications, we took the additional precaution of preparing the tosylhydrazone of ketone **9** using deuterated tosylhydrazine and solvent.

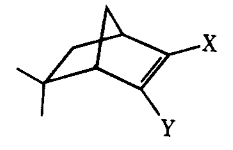
Carbene formation was effected by either thermal (dry salt, 160–180 °C at 0.1 Torr) or photochemical (450-W high-pressure lamp, THF, 25 °C) decomposition of tosylhydrazone **7a**. The 3,2-hydride shift product, 5,5-dimethylnorbornene (**11a**) was formed as the sole volatile product in 75% (thermal) and 50% (photochemical) yields. When the deuterated tosylhydrazones were decomposed, all the deuterium was found to reside in the olefinic positions in the product alkene. Since the olefinic protons are not differentiated by NMR at 100 Hz, 5,5-dimethylnorbornene was converted to the exo epoxide by treatment with peracetic acid. The deuterium distribution in **11** was then easily determined, since the corresponding epoxide protons have different chemical shifts (C-2, τ 7.04; C-3, 6.90). The NMR data along with low voltage mass spectral analyses of product 5,5-dimethylnorbornene are given in Table I. These data were then used to calculate product composition in terms of monodeuterated alkenes **11b** and **11c** (Table II).



7b

10

12



11a, X = Y = H
b, X = D; Y = H
c, X = H; Y = D

The results of Table II show that the stereoselectivity of hydride migration in both the thermal and photolytic decompositions is about 95:5 exo/endo. Thus, instead of the greater than 100:1 exo/endo selectivity found in the norbornyl cation, the carbene selectivity is approximately 20:1, which is in rather close agreement with the ratio (13) observed with **2**[10] and contrasts with the exo/endo migration ratio of 138 observed for **3**.[11]

The product formation observed in this analysis is assumed to be that due to a singlet state carbene intermediate, since evidence has been presented which suggests that triplet carbenes do not undergo hydrogen migration.[16] Some experimental support for this view was obtained by irradiating tosylhydrazone **7a** in the presence of benzophenone sensitizer (Pyrex filter); nitrogen was evolved (ca. 1 equiv), but the yield of 5,5-dimethylnorbornene dropped dramatically to less than 5%. If one assumes a single product determining intermediate, the observation of significant endo hydride migration argues against delocalization of the C-1–C-6 σ bond, for this would require a front side displacement of C-2 in the hydride migration transition state. A significant advantage of an analysis of hydrogen migration in 2-carbena-6,6-dimethylnorbornane (**12**) relative to carbene **3** is the local symmetry of the exo and endo C-3–H bonds with respect to the empty p orbital at C-2. As a consequence, there should be no preference for either exo or endo hydrogen migration based upon orbital overlap considerations.[17] The intramolecular relationships should, in fact, be closely similar to a classical 2-norbornyl cation, where torsional effects have been estimated to favor exo over endo C-3–C-2 hydride migration by a maximum of 6 kcal/mol.[18] One would expect considerably less difference than this maximum for the transition states for the 2-carbenanorbornane intermediate under consideration, however, since the isotope effects, $k_H/k_D = 0.90 \pm 0.18$ for thermolysis and $k_H/k_D = 0.84 \pm 0.18$ for photolysis,[19] found in the present instance and the small values previously observed for β C–H migration (k_H/k_D = 1.1–1.4) in diazoalkane decompositions[11,20,21] suggest that hydrogen bridging is not well developed in the migration step. Therefore, on the basis of the present evidence, we conclude that small differences in torsional interactions in the transition states for exo and endo hydride migration, rather than σ-bond delocalization, are responsible for the stereoselectivity observed for 2-carbene-6,6-dimethylnorbornane.

Experimental Section

Melting points were determined using a Büchi melting point apparatus and are uncorrected. All boiling points are also uncorrected. Infrared spectra were recorded on either a Beckman IR-9 infrared spectrophotometer or a Perkin-Elmer 621 infrared spectrophotometer. Proton NMR spectra were recorded on a Varian Associates A-60 or HA-100 NMR spectrometer. Mass spectra were run on an Atlas CH-7 or Finnigan 1015 S/L mass spectrometer. Elemental analyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, 5251 Elback Uber Engelskirchen, Fritz-pregl-strasse 14-26, West Germany. VPC analyses were carried out with an F and M Model 700 Chromatograph equipped with dual columns and thermal conductivity detectors. The following columns were used: (1) 10 ft × 0.25 in. aluminum containing 10% Carbowax 20M on Anakrom 70–80 ABS; (2) 8 ft × 0.25 in. aluminum containing 8% Carbowax 20M on Anakrom 70–80 ABS; (3) 8 ft × 0.25 in. aluminum 5% OV-17 on 60–80 Chromosorb G; (4) 9 ft × 0.25 in. aluminum containing 10% Carbowax 20M and 1% XF-1150 on Anakrom 70–80 ABS; (5) 18 ft × 0.125 in. stainless steel containing 10% UCW-98 on 80–100 Diatoport S. Products ratios and percentage yields calculated from chromatographic data are based on relative peak areas as measured by a Hewlett-Packard 3373B Integrator.

Preparation of 5,5-Dimethyl-2,3-*exo*-epoxynorbornene (4). The procedure of Donaldson[13] was used with only minor modifications. Sublimation of the resulting product (20 Torr, pot temperature 70 °C) yielded the title compound in 75% yield; NMR (CCl_4, 100 MHz) δ 3.10 (doublet of doublets, J = 3.5, 0.7 Hz, 1 H, C-3 proton), 2.96 (doublet of doublets, J = 3.5, 0.7 Hz, 1 H, C-2 proton), 2.34 (unresolved, 1 H, bridgehead C-1 proton), 1.90 (broadened singlet, 1 H, bridgehead C-4 proton), 1.34 (broadened doublet, J = 4 Hz, 1 H, exo-C-6 proton), 1.22 (broadened doublet, J = 4 Hz, 1 H, endo-C-6 proton), 1.15 to 0.80 (complex signals including two singlets for the two methyl groups on C-5 at δ 1.05 and 1.02, 8 H).

Preparation of 6,6-Dimethylnorbornan-2-ol. The procedure of Donaldson[13] was used. Purification by preparative VPC yielded NMR (CCl_4, 100 MHz): δ 4.07 (doublet, J = 6 Hz, 1 H, proton α to hydroxyl), 2.20 (multiplet, 1 H, proton on C-4), 1.68 (singlet, 1 H, C-1 bridgehead proton), 1.63 to 0.73 (complex series of absorptions including methyl singlets at δ 1.00 and 0.97, 12 H).

Preparation of *endo*-3-Deuterio-6,6-dimethylnorbornan-2-ol (5a). The reaction was run as described[13] except that 3 equivalents of lithium aluminum deuteride (99.5% *d*) was heated at reflux with **4** for 3 days. After workup, VPC analysis on column 1 showed the product to consist of a mixture of alcohol and epoxide in a ratio of 70:30.

Analysis of the extent of deuteration was carried out by treating alcohol **5a** (0.23 g, 0.0016 mol) with 1 mL of Me_2SO and 0.4 mL of Trisil (Pierce Chemical Co.). The mixture was shaken for 5–10 min and left undisturbed overnight. The organic layer was separated, and the Me_2SO layer was extracted once with hexane. The organics were combined and washed once with H_2O, then dried over $CaCl_2$. The trimethylsiloxynorbornane derivative was purified by preparative VPC (column 2). Low voltage mass spectrum showed $\%D_1$ as 97.8 ± 0.1%. There was no D_2.

Preparation of 6,6-Dimethylnorbornan-2-one (6). 6,6-Dimethylnorbornan-2-ol was oxidized by the procedure of Donaldson.[13] Distillation of the title ketone (bp 80–83 °C, 18 Torr; lit. bp 74–75 °C, 12 Torr) yielded 51.5% (calculated from epoxide **4**); NMR (CCl_4, 100 MHz): δ 2.75 (unresolved, 1 H, bridgehead proton at C-4), 2.02 (slightly, broadened singlet, C-1 bridgehead), 1.97–0.80 (complex absorptions including methyl singlets at δ 1.07 and 0.96, 12 H).

Oxidation of *endo*-3-Deuterio-*exo*-6,6-Dimethylnorbornan-2-ol. The crude mixture of **5a** and **4** was treated with chromic acid in acetone as described.[13] Distillation yielded **6**.

Deuteration of 6,6-Dimethylnorbornan-2-one. The title ketone (1.0 g) was dissolved in 25 mL of methanol-O-*d* (99% d_1) with a catalytic amount of sodium methoxide and stirred for 2 h at room temperature. After quenching with D_2O and dilution with water, the solution was extracted with pentane. The pentane was washed with water and brine and dried over sodium sulfate. After removal of most of the pentane by distillation, the ketone was used without further purification for the preparation of tosylhydrazone. Samples for spectral analysis were separated using VPC column 3. The extent of deuteration at the exo and endo C-3 position was determined by NMR aided by a lanthanide induced shift. $Eu(fod)_3$ was added until the difference between the exo, endo, and bridgehead positions became large enough to permit accurate determination of the relative areas. The bridgehead hydrogen (C-1) was used as the standard. When the bridgehead hydrogen was at δ 10.34, the exo-3 and endo-3 protons absorbed at δ 10.77 and 10.03, respectively.

Preparation of 6,6-Dimethyl-2-norbornanone *p*-Toluenesulfonylhydrazone. A mixture of 4.5 g (0.033 mol) of 6,6-dimethylnorbornan-2-one and 6.2 g (0.033 mol) of tosylhydrazine in 35 mL of 95% ethanol with 2 drops of concentrated hydrochloric acid was heated at reflux for 3 h. Several milliliters of water was added, and the solution was cooled to room temperature, then placed in a refrigerator, yielding 5.1 g (0.017 mol), 51%, mp 150–154 °C. Recrystallization from ethanol yielded mp 157.5–159 °C; IR (0.1 mm, $CHCl_3$): 3200 cm^{-1} (m, N–H stretching), 1662 (m, C=N stretching), 1598 (m, aromatic C=C stretching) and 1170 (s, SO_2–N stretching); NMR (100 MHz, $CDCl_3$): δ 7.89 (singlet, 1 H, N–H), δ 7.84 and 7.26 (each a doublet, 2 H each, aromatic protons), δ 2.38 (singlet, 3 H, aromatic methyl), δ 2.34 (multiplet, 2 H, C-1 and C-4 bridgehead protons), δ 2.2 to 1.2 (complex signals, 5 H), δ 0.96 (1 H, buried under methyl) δ 0.96 and 0.56 (singlets, 3 H each, methyls on C-6).

Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.71; H, 7.24. Found: C, 62.70; H, 7.21.

Preparation of *endo*-3-Deuterio-6,6-dimethylnorbornan-2-one Tosylhydrazone. This preparation was carried out in a manner identical with that described above for the undeuterated tosylhydrazone. Recrystallization from methanol gave mp 156.5–158 °C.

Preparation of *exo*-3-Deuterio-6,6-dimethylnorbornan-2-one Tosylhydrazone. The exo-deuterated ketone (about 1 g, 0.08 mol) was placed in 10 mL of methanol-*O-d* (99% d_1) with 1.5 g (0.08 mol) of tosylhydrazine (previously recrystallized from methanol-*O-d*) and a drop of DCl in D_2O. The solution was heated at reflux for 3 h; D_2O was added, and the solution was allowed to cool to room temperature, then placed in a refrigerator. The crystalline product was recrystallized from methanol-*O*-*d*-D_2O yielding purified tosylhydrazone with mp 156–158°.

Dry Salt Pyrolysis of the Lithium Salt of 6,6-Dimethylnorbornan-2-one Tosylhydrazone. A 25-mL flask was charged with 306 mg (1.00 mmol) of tosylhydrazone. To this was added 10 mL of anhydrous ether, and then 450 μL of 2.2 M methyllithium in ether (1.0 mmol) was added to the solution with swirling. When gas evolution ceased, the ether was evaporated by blowing dry nitrogen over the solution while swirling. When most of the ether had evaporated, the white lithium salt covered the inside of the flask. The salt was then warmed to 40 °C and any remaining volatile material was pumped off at 0.1 Torr. The dry salt was then placed in an oil bath maintained at 180 °C, pressure 0.1 Torr, and the volatile products were collected in a trap maintained at −78 °C. After 1 h the volatile material in the trap was washed out with pentane, and the resulting pentane solution was analyzed by VPC on columns 1, 4, and 5. Only one product was detectable by VPC, and it had IR, NMR, and VPC retention time identical with 5,5-dimethylnorbornene. The yield (internal VPC standard) was 75%.

Irradiation of the Lithium Salt of 6,6-Dimethylnorbornan-2-one Tosylhydrazone. In a 50-mL flask, 306 mg (1.00 mmol) of tosylhydrazone was dissolved in 25 mL of tetrahydrofuran (which had been freshly distilled from lithium aluminum hydride) and 95 mg of decane (for VPC internal standard). Methyllithium (460 μL of 2.2 M, 1.0 mmol) in ether was added with stirring at 0 °C. A small aliquot was withdrawn and set aside, and the rest was irradiated with a 450-W Hanovia high-pressure mercury lamp until the theoretical amount of nitrogen was evolved and evolution stopped. The solution was then diluted with 200 mL of water and extracted with 5 × 15 mL of pentane. The pentane extracts were combined, washed with 5 × 250 mL of water and 1 × 100 mL of brine and dried over anhydrous sodium sulfate. The solution was concentrated by distilling off most of the solvent through a Vigreux column. VPC analysis on column 5 showed there were two peaks other than the decane internal standard. The peak with the shorter retention time, formed in variable yield, had VPC retention time and infrared identical with that of toluene. The other peak had VPC retention time, IR, and NMR identical with 5,5-dimethylnorbornene. Internal VPC standard indicated the yield to be 50%. The aliquot set aside was worked up in an identical manner as the irradiated mixture, and VPC analysis indicated there was no (<0.1%) alkene formed by methyllithium elimination.[22]

Irradiation of the Lithium Salt of 6,6-Dimethylnorbornan-2-one Tosylhydrazone in the Presence of Benzophenone. To a solution of the lithium salt in tetrahydrofuran as described above was added 1.0 equivalent of reagent grade benzophenone. The solution was irradiated through a Pyrex filter until nitrogen evolution ceased (approximately 1 equiv). After workup similar to that described above, VPC analysis on column 5 gave a low yield (<5%) of 5,5-dimethylnorbornene as the only volatile product.

Decomposition of Deuteriated Tosylhydrazones. Deuterated tosylhydrazones were decomposed in exactly the same manner as described above for undeuterated tosylhydrazones.

Preparation of Deuterated 4 for NMR Analysis. Deuterated 5,5-dimethylnorbornene, formed from tosylhydrazone decompositions in runs 1–5, was collected by preparative VPC (usually ca. 20 mg), and placed in a small vial with 50 μL of chloroform, 250 μL of 40% peracetic acid, and 5 mg of anhydrous sodium acetate. After warming to 40 °C for 5 min, the solution was diluted with 2 mL of water, and 250 μL of 40% sodium hydroxide was added with cooling. The solution was then extracted 3 times with 200 μL of pentane. The pentane extracts were washed with 500 μL of water and 200 μL of brine and dried over anhydrous sodium sulfate. Epoxide 4 was then collected by preparative VPC and subjected to NMR analysis.

NMR Analysis of Deuterated 4. Epoxide **4**, generated as described above from the deuterated alkene **11a** produced in runs 1–5, was subjected to NMR analysis in CCl_4 at 100 MHz. Integration of the absorptions at δ 3.10 and 2.96 due to the protons at C-3 and C-2 was compared with the integration of the signals at δ 2.34 and 1.90 due to the C-1 and C-4 bridgehead protons. In all cases, the deuterium content was found to be, within experimental error, the same as the deuterium content determined by mass spectral analysis. The ratio of the areas under the peaks at δ 3.10 and 2.96 yielded, after correcting for the amount of undeuterated alkene (available from mass spectral analysis), the ratio of products **11b** and **11c**. The integrals are given in Table I and the calculated ratios of products are given in Table II.

Mass Spectral Analysis of Deuterated 11a. Deuterated 5,5-dimethylnorbornene from runs 1–5 was collected by preparative VPC and subjected to mass spectral analysis at low ionizing potentials. At 14 eV the parent − 1 ion had been reduced to <0.5%. The peak heights, after correcting for the natural abundance of C-13, yielded the amounts of d_0, d_1, and d_2. These values are presented in Table I.

Registry No.—**4**, 63089-27-0; **5a**, 63089-28-1; **6**, 63089-29-2; **7a**, 63089-30-5; **7b**, 63089-31-6; **9**, 63089-32-7; **10**, 63089-33-8; **11b**, 63089-34-9; **11c**, 63089-35-0; 6,6-dimethylnorbornan-2-ol, 63122-47-4; 6,6-dimethyl-2-norbornone tosylhydrazone, 58728-89-5; *endo*-3-deuterio-6,6-dimethylnorbornan-2-one tosylhydrazone, 63089-36-1; *exo*-3-deuterio-6,6-dimethylnorbornan-2-one tosylhydrazone, 63089-37-2; 5,5-dimethylnorbornene, 497-28-9.

References and Notes

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