Table IV. Relative Rate Determinations

substrate	k_{rel}	substrate	k_{rel}
1h	0.16	**1e**	1.00
1g	0.91	**1b**	2.07
1c	1.9	**1b**	1.00
1f	1.0	**1a**	10.5
1f	0.79		
1d	1.00		
1e	3.02		

of **1** solutions with concentrations ranging from 0.1 to 0.25 M was prepared prior to the spectral measurements. After base-line correction, the spectrum was measured from 450 to 750 nm. During the entire procedure, the solution was carefully protected from room light to avoid photochemically initiated reactions. The absorbance at the maximum of the charge-transfer band (λ_{max}) was used as described in eq 3. The results are gathered in Table II.

Absolute Rate Constant Determinations. All thermal reactions were carried out in sealed tubes at 190 °C unless otherwise noted. The Pyrex tubes were base-washed using a procedure previously described.[24] Thus, the Pyrex tubes were initially washed with 1 N HCl for 24 h and then 1 N NaOH for an additional 24 h. The tubes were then rinsed extensively with distilled H_2O and then CH_3OH. The tubes were then dried at 110 °C. All operations involving sample preparation and analyses were carefully performed in the dark to ensure that the observed products were due to thermal reaction and not to photochemical reactions. A solution of **1** (0.100 mmol), DDQ (0.100 mmol), and the internal standard in 10.0 mL of freshly distilled acetonitrile was prepared and added to several Pyrex tubes. These tubes were degassed using three freeze-pump-thaw degassing cycles and then sealed under vacuum. The sealed tubes were placed in a Neslab Model EX250-HT constant-temperature bath for the designated time. The product mixtures were then analyzed directly on the GLC and HPLC.

Relative Rate Constant Determinations. The compounds were divided into four groups in order to minimize the relative rate differentials between the fastest and the slowest reacting compounds. A solution of 0.01 M **1**, internal standard, and 0.01 M DDQ in freshly distilled acetonitrile were placed in base-washed Pyrex tubes and sealed as described above. The tubes were placed in an oil bath at 190 °C. The relative rates were determined by withdrawing the tube from the oil bath and measuring the conversion amounts relative to the internal standard. The amount of conversion was kept below 30% to ensure that the data did not reflect an artificial competition. A minimum of three separate conversion amounts was averaged to yield the results reported in Table IV. In all cases, the relative rates were consistent over the three conversion yields.

Acknowledgment. We gratefully acknowledge the financial support of the Consortium for Fossil Fuel Liquefaction Science for the completion of this work.

Registry No. **1a**, 19962-28-8; **1b**, 19962-27-7; **1c**, 19962-26-6; **1d**, 946-80-5; **1e**, 19962-23-3; **1f**, 19962-25-5; **1g**, 20600-22-0; **1h**, 57928-75-3; DDQ, 84-58-2; TCNE, 670-54-2; 4-$MeOC_6H_4CH_2Cl$, 824-94-2; 4-$MeC_6H_4CH_2Cl$, 104-82-5; 4-$FC_6H_4CH_2Cl$, 352-11-4; $PhCH_2Cl$, 100-44-7; 3-$MeOC_6H_4CH_2Cl$, 824-98-6; 4-$ClC_6H_4CH_2Cl$, 104-83-6; 4-$BrC_6H_4CH_2Cl$, 589-17-3; 4-$NCC_6H_4CH_2Cl$, 874-86-2; PhONa, 139-02-6; 4-$MeOC_6H_4CD_2OPh$, 124781-14-2; $PhCD_2OPh$, 124781-15-3.

An Anomalous Simmons–Smith Reaction of an Alkene To Form an Iodomethyl Derivative

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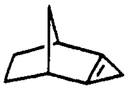
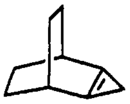
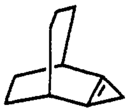
An anomalous type of product from a Simmons–Smith reaction, involving the addition of the groups H and CH_2I across the double bond, has been observed. When older samples of zinc–copper couple and diiodomethane are used in the reaction of 2-chloronorbornene (**6**), *endo*-2-chloro-*exo*-3-(iodomethyl)norbornane (**7**) is formed. Chloride **6** does proceed sluggishly via the classic reaction when fresh reagents are used, giving cyclopropanation to **4**. Chloride **6** also is reluctant to add a methylene group via palladium(II) acetate catalysis when generated from diazomethane, giving poor yields of cyclopropyl chloride **4**. Dehydrohalogenation of chloro iodide **7** was also studied, the main product being *endo*-2-chloro-*exo*-3-methylenenorbornane (**8**), though isomerization to 2-chloro-3-methylnorbornene (**5**) also occurs. Gas chromatography at higher temperatures with a certain packed column also isomerizes **8** to **5** and forms some *exo*-2-chloro-3-methylenenorbornane (**9**).

Recently we have become interested in synthesizing tricyclic cyclopropenes such as **1**, **2**, and **3** for the synthetic challenge and to see if some interesting strained olefin chemistry would be demonstrated by studying these compounds. A number of routes are being investigated.[1] In the early stages of our work on the synthesis of **1** we were interested in making the cyclopropyl chloride **4** (Scheme I). Szeimies has had success synthesizing a number of highly strained cyclopropenes by dehydrohalogenations of cyclopropyl chlorides,[2] so we thought this to be a reasonable approach to use. We also wanted 2-chloro-3-methylnorbornene (**5**), since Gassman synthesized a bicyclic cyclopropene by an alkyllithium-induced γ-elimination of HCl from 1-chloro-2-methylcyclohexene.[3]


1


2


3

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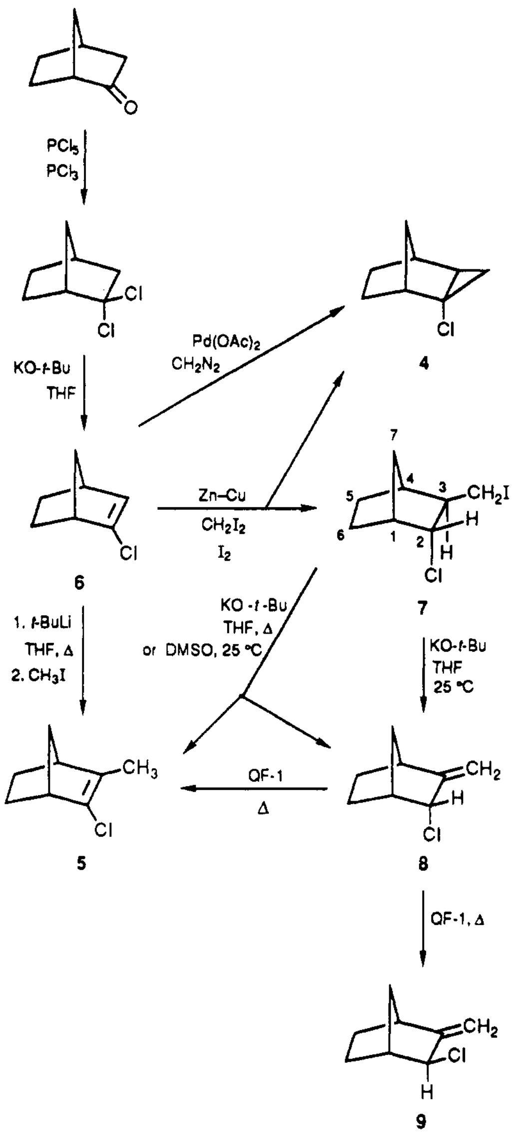
[1] For a successful synthesis of olefin **2**, see: Chenier, P. J.; Southard, D. A., Jr. *J. Org. Chem.* **1989**, *54*, 3519. See also: Chenier, P. J.; Southard, D. A., Jr. *Ibid.*, submitted for publication.

[2] (a) Szeimies-Seebach, U.; Schöffer, A.; Römer, R.; Szeimies, G. *Chem. Ber.* **1981**, *114*, 1767. (b) Zoch, H.-G.; Szeimies, G.; Römer, R.; Germain, G.; Declercq, J.-P. *Ibid.* **1983**, *116*, 2285. (c) Harnisch, J.; Baumgärtel, O.; Szeimies, G.; Meerssche, M. V.; Germain, G.; Declercq, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 3370. (d) Szeimies, G.; Baumgärtel, O. *Chem. Ber.* **1983**, *116*, 2180. (e) Baumgärtel, O.; Harnisch, J.; Szeimies, G.; Meerssche, M. V.; Germain, G.; Declercq, J.-P. *Ibid.* **1983**, *116*, 2205. (f) Schlüter, A.-D.; Harnisch, H.; Harnisch, J.; Szeimies-Seebach, U.; Szeimies, G. *Ibid.* **1985**, *118*, 3513.

[3] (a) Gassman, P. G.; Valcho, J. J.; Proehl, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 231. (b) Gassman, P. G.; Valcho, J. J.; Proehl, G. S.; Cooper, C. F. *Ibid.* **1980**, *102*, 6519.

Scheme I



2-Chloronorbornene (**6**) is known and has been made in two steps from norcamphor.[4,5] We thought addition of a methylene group would easily provide us with a convenient route to the cyclopropyl chloride **4**. We thought that vinyl chloride **6** would easily react with a methylene group either via the classic Simmons–Smith reaction utilizing diiodomethane and zinc–copper couple[6] or newer methods such as palladium(II)-catalyzed additions of diazomethane.[7,8]

Results and Discussion

Having had experience with the Simmons–Smith reaction of norbornene derivatives,[9] we set out to study this reaction first. During three attempts at this reaction on 2-chloronorbornene (**6**), little or no Simmons–Smith product was obtained with the usual procedure when older bottles of both diiodomethane and zinc–copper couple were used. A product with a boiling point much higher than expected for **4** and spectral data that were in accord with *endo*-2-chloro-*exo*-3-iodomethylnorbornane (**7**) was formed. The ^{1}H NMR spectrum shows a triplet at δ 3.67 for the *exo*-2-hydrogen. The coupling constant of 4.2 Hz is reasonable for the bridgehead-exo (usually 3–4 Hz[10]) and the 2,3-trans (usually 2–5 Hz[10]) couplings. In norbornyl systems the trans coupling is much smaller than the cis coupling by a dihedral angle effect.[10] The two protons of the iodomethyl group appear as a doublet at δ 3.10 with a vicinal coupling of 8.0 Hz to the *endo*-3-hydrogen. Irradiation of the bridgehead proton at δ 2.49 collapses the *exo*-2-hydrogen to a doublet, establishing conclusively the stereochemistry of the chlorine as endo. Irradiation at δ 1.92 collapses the triplet of the *exo*-2-hydrogen to a doublet and the doublet of the CH_2I to a singlet, thus pointing to this region as the *endo*-3-hydrogen. The ^{13}C NMR spectrum is equally confirming for chloro iodide **7**, showing eight carbons. A refocused INEPT experiment reveals four methine groups downfield from δ 42 to 67 and four methylene groups upfield from δ 8 to 35. The absorption at δ 8.4 is no doubt the CH_2I group shielded by the heavy atom effect of the iodine. High-resolution mass spectrometry showed the expected exact mass for **7**.

When newer bottles of diiodomethane and zinc–copper couple are used, the reaction of chloride **6** becomes very sluggish. No chloroiodide is formed, and mostly starting material is recovered after a 2-day reflux with excess reagents. Only 17% of cyclopropyl chloride **4** is formed. After 7 days with an even greater excess of reagents, only 18% of **4** was formed. The cyclopropyl chloride could not be separated by distillation from the olefinic chloride and had a more expected boiling point than the chloroiodide. Gas chromatography was employed to purify **4**. Chloride **4** had no protons downfield of δ 2.6 while still having eight carbons from δ 11 to 47. Exo attack is presumed, since this is the case for other norbornene derivatives.[9] The chloro iodide was not detected whenever new bottles of diiodomethane and zinc–copper couple were used. The slow reactivity of chloroalkenes has to our knowledge not been noted before for the Simmons–Smith reaction. Indeed an examination of the literature has shown that good examples of the reaction are lacking when a halogen is present on the double bond. Apparently the withdrawing effect of the chlorine makes the π cloud less nucleophilic so that the reaction is not successful, though norbornene and norbornadiene have been reported to undergo the reaction, as does methyl norbornene-1-carboxylate.[9] It is known that the Simmons–Smith cyclopropanation is accelerated by electron-donating substituents at the double bond and retarded by electron-withdrawing groups.[11]

We then decided to try to improve the synthesis of cyclopropyl chloride **4** by using the palladium acetate catalyzed addition of a methylene group generated from diazomethane. This has been reported to proceed well for

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(4) Bixler, R. L.; Niemann, C. *J. Org. Chem.* **1958**, *23*, 742.

(5) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 1348.

(6) For reviews, see: (a) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 1. (b) Hashimoto, H. *Yuki Gosei Kagaku Kyokai Shi* **1976**, *34*, 246. (c) Conia, J. M. *Pure Appl. Chem.* **1975**, *43*, 317. (d) Kaltenberg, O. P. *Wiad. Chem.* **1972**, *26*, 285. (e) Sawada, S. *Bull. Inst. Chem. Res., Kyoto Univ.* **1969**, *47*, 451. (f) Tsuji, T.; Nishida, S. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley and Sons: New York, 1987; Chapter 7.

(7) We thank M. P. Doyle, Trinity University, San Antonio, TX, for suggesting this reaction to us.

(8) (a) Kottwitz, J.; Vorbrüggen, H. *Synthesis* **1975**, 636. (b) Mende, U.; Radüchel, B.; Skuballa, W.; Vorbrüggen, H. *Tetrahedron Lett.* **1975**, 629. (c) Castanet, Y.; Petit, F. *Ibid.* **1979**, 3221. (d) Suda, M. *Synthesis* **1981**, 714.

(9) (a) Chenier, P. J.; Kiland, P. J.; Schmitt, G. D.; VanderWegen, P. G. *J. Org. Chem.* **1980**, *45*, 5413. (b) Chenier, P. J.; Cristie, D. M.; Goettl, V. M. *Ibid.* **1985**, *50*, 3213. (c) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

(10) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969; p 289.

(11) See ref 6f, p 321. See also: (a) Blanchard, E. P.; Simmons, H. E. *J. Am. Chem. Soc.* **1964**, *86*, 1337. (b) Rickborn, B.; Vhan, J. H.-H. *J. Org. Chem.* **1967**, *32*, 3576.

Scheme II

$$7 \xrightarrow[\substack{\text{THF} \\ 25\ ^\circ\text{C}}]{\text{KO-}t\text{-Bu}} 8$$

$$7 \xrightarrow[\substack{\text{THF} \\ \text{reflux}}]{\text{KO-}t\text{-Bu}} \underset{43\%}{5} + \underset{57\%}{8}$$

$$7 \xrightarrow[\substack{\text{DMSO} \\ 25\ ^\circ\text{C}}]{\text{KO-}t\text{-Bu}} \underset{37\%}{5} + \underset{63\%}{8}$$

$$5 + 8 \xrightarrow[\Delta]{\text{QF-1}} 5 + 8 + 9 + \text{"X"}$$

norbornene and norbornadiene.[8a] Here too the reaction of chloride **6** remains slow. Even with larger amounts of catalyst and 4 days of stirring with diazomethane in ether the cyclopropyl chloride **4**:olefinic chloride **6** ratio did not increase over 32:68.

The treatment of chloro iodide **7** with base proved interesting (Scheme II). Potassium *tert*-butoxide in dry tetrahydrofuran (THF) at 25 °C gave a single product, *endo*-2-chloro-3-methylenenorbornane (**8**), by preferential elimination of HI rather than HCl and formation of the exocyclic double bond rather than a norbornene double bond. The ^{13}C NMR spectrum for **8** shows the expected peaks, including a nonprotonated olefinic carbon (via refocused INEPT) at δ 154.8 and an olefinic methylene group at 106.9. Three other methylene and three methine absorptions, with the CHCl occurring at 63.4, complete the spectrum. The structure is further confirmed by the ^1H NMR spectrum, showing the two vinyl hydrogens downfield at δ 4.9–5.1 and the *exo*-2-hydrogen at 4.4–4.6, together with the two bridgehead hydrogens at 2.7–2.9 and 2.3–2.6. Irradiation of the bridgehead hydrogen at 2.5 affects the *exo*-2-hydrogen. Although this hydrogen is a multiplet, a small doublet at its top (J = 2.2 Hz) disappears, proving the bridgehead to *exo*-2-hydrogen interaction.

When potassium *tert*-butoxide in THF is refluxed for 24 h with chloro iodide **7** the dehydrohalogenation is more complex. In addition to **8**, 2-chloro-3-methylnorbornene (**5**) is also formed. ^1H NMR studies and gas chromatography (capillary SE-54, FID detection) showed a **5**:**8** ratio of 43:57. When chloro iodide **7** is treated with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) at 25 °C, almost the same **5**:**8** ratio of 37:63 is observed by ^1H NMR spectroscopy. This is probably near the equilibrium value for these conditions, with the extra temperature being necessary in the THF to reach this point, whereas in DMSO it is reached at 25 °C.

The structure of **5** was proven by comparison of its spectra with an authentic sample[12] and by our independent synthesis via methylation of chloride **6**. The singlet methyl absorption at δ 1.66 dominates the ^1H NMR spectrum of **5**, and the eight carbons of the ^{13}C NMR spectrum include the two olefinic carbons at 138.0 and 130.2, both of which are nonprotonated by INEPT.

A complication in the analysis of this reaction is the fact that, although products **5** and **8** are stable to a capillary SE-54 column up to 200 °C, an attempt to analyze or collect them from a packed QF-1 column failed because of isomerization. The ratio of **5**:**8** that is registered through the packed column varies from 51:49 at 105 °C to 100:0 at 197 °C. A further complicating factor is that a unidentified compound "X" also increases in amount as the temperature is raised, and becomes nearly 35% as a mixture with **5** when the column is at 197 °C (see Table I, Experimental Section). When a small amount of starting mixture is heated in a sealed tube to 200 °C for 0.5 h, no thermal isomerization takes place. Thus the QF-1 is taking an active part in this isomerization.

Table I

temp °C	% **5** (t_R, min)	% **8** (t_R)	% "X" (t_R)	**5**:**8**
none			none	42.7:57.3
105	49.5 (16.5)	47.3 (26.0)	3.1 (14.0)	51.1:48.9
139	61.2 (9.0)	34.8 (13.0)	4.0 (8.0)	63.7:36.3
172	75.1 (6.5)	10.4 (8.5)	14.5 (5.5)	87.9:12.1
197	65.2 (6.0)	0	34.8 (5)	100:0

Finally, when some **8** is collected after chromatographing through QF-1, the exo chloride isomer **9** is also indicated. Instead of the CHCl proton at δ 4.56 as in **8**, there is an additional absorption at 4.21. Since endo protons are usually upfield compared with exo protons in norbornyl derivatives, the shift of 4.56 to 4.21 for the endo proton of exo chloride **9** is in accord with this phenomenon. A new CH_2= absorption at 5.12 (instead of 4.99) indicates further evidence for epimerization to **9**. The ^{13}C NMR spectrum also shows new shifts for seven of the eight carbons. Both exo and endo chlorides **9** and **8** have been made, but no spectral or physical properties have been reported.[8c,13] Thus via base and GC the endo chloride **8** can isomerize to methyl chloride **5**, and on the GC column **8** also forms exo chloride **9** and compound "X".

In summary, it is important to note that the use of older or oxidized reagents in the Simmons–Smith reaction can lead to iodomethyl derivatives of olefins. This has not been reported before for this classic reaction. We plan no further work in this area, but it would be interesting to see if this unique addition of the groups H and CH_2I across the double bond could be made synthetically useful. Although we did no further testing of the zinc–copper couple used in our first experiments, and the older bottle of diiodomethane was used up, we strongly suspect the diiodomethane as being most instrumental at causing this anomalous Simmons–Smith reaction. The bottle in question was a distinct orange color, it turned the solution dark upon mixing with chloride **6**, and the final color of the solution after reflux was a darker gray. Perhaps this reaction only competes when the starting olefin is not too reactive, as in our case. Other workers should beware of this possible reaction when using these conditions in attempted cyclopropanations.

Experimental Section

The following instruments were used: an IBM NR80AF FT-NMR spectrometer, Nicolet 5DXC FT-IR and Perkin Elmer 1420 IR spectrophotometers, and Hewlett-Packard 5890 FID and Varian Aerograph 700 Autoprep TCD gas chromatographs with helium as carrier gas. NMR data are given in parts per million relative to Me_4Si. ^1H and ^{13}C NMR spectra were obtained at 80 and 20 MHz, respectively. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Mass spectra were taken by the Department of Chemistry, University of Minnesota, Minneapolis, MN.

2-Chloronorbornene (6) was prepared in two steps from norcamphor.[4,5]

***endo*-2-Chloro-*exo*-3-(iodomethyl)norbornane (7)** (formed when older bottles of diiodomethane and zinc–copper couple are

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[12] We thank P. G. Gassman and I. A. Gennich, University of Minnesota, for furnishing these spectra.

[13] (a) Petit, F.; Castanet, Y. *J. Mol. Catal.* **1986**, *35*, 143. (b) Godleski, S. A.; Gundlach, K. B.; Yo, H. Y.; Keinan, E.; Froloir, F. *Organometallics* **1984**, *3*, 21. (c) Petit, F.; Castanet, Y. *J. Chem. Res.* (*S*) **1982**, 238; *J. Chem. Res.* (*M*) **1982**, 2401.

employed). Zinc–copper couple (151.1 g, 2.31 mol), iodine (15.4 g), and anhydrous ether (500 mL) were stirred until the iodine color faded. Diiodomethane (349.6 g, 1.31 mol) and 2-chloronorbornene (**6**, 140.0 g, 1.09 mol) were added in anhydrous ether (200 mL) dropwise over 1 h. The mixture was refluxed for 40 h. The usual workup for such reactions[9a] gave a mixture with approximately one-third of starting material left. The mixture was reacted again with more reagents in amounts identical to the first run. Vacuum distillation of the final mixture gave 54.3 g of a first fraction with bp 31–95 °C (1.4–1.6 mm) which contained unreacted **6**, cyclopropyl chloride **4**, and chloro iodide **7**. A second fraction with bp 98–119 °C (1.6 mm) contained *endo*-1-chloro-*exo*-3-(iodomethyl)norbornane (**7**) (39.8 g, 0.147 mol, 13%). Gas chromatography (SE-54, 150 °C) showed the material to be 74% pure. The iodide was redistilled and showed 91.2% purity by GC: bp 105 °C (1.3 mm); IR (neat) 2958, 2874, 1454, 1427, 1308, 1237, 1181, 949, 912, 835, 787, 756, 604, 575 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.67 (t, 1 H, CHCl, J = 4.2 Hz), 3.10 (d, 2 H, CH_2I, J = 8.0 Hz), 2.3–2.6 (m, 1 H, bridgehead-C-1), 2.1–2.3 (m, 1 H, bridgehead-C-4), 0.9–2.1 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 66.9 (d), 55.5 (d), 44.7 (d), 42.7 (d), 35.0 (t), 29.3 (t), 21.3 (t), 8.4 (t); MS (EI, 30 eV, 150 °C) *m/e* (%) 270 (M^+, small), 135 (12), 107 (C_8H_{11}, 72), 93 (13), 91 (20), 79 (100), 67 (22), 41 (13); HRMS calcd for $C_8H_{12}ClI$ 269.9670, found 269.9694.

***endo*-2-Chlorotricyclo[3.2.1.0^{2,4}]octane (4) via the Simmons–Smith Reaction** (formed when newer bottles of diiodomethane and zinc–copper couple are employed). Using the same procedure as above with fresh zinc–copper couple[14] (19.62 g, 300 mmol), fresh diiodomethane[15] (45.4 g, 169.6 mmol), iodine (2.0 g), olefinic chloride **6** (13.85 g, 106.1 mmol), and anhydrous ether (100 mL) in a 7-day reflux followed by the standard workup showed a mixture of **6** and product cyclopropyl chloride **4**, but no iodide **7**. Vacuum distillation with slowly decreasing pressure gave bp 62 °C (55 mm)–114 °C (1.7 mm). Both **6** and **4** were in all four fractions taken. Total distilled material was 3.16 g, only 18% of it being **4**. A pure sample of **4** was collected by GC (QF-1, 129 °C): ^{1}H NMR ($CDCl_3$) δ 2.4–2.6 (m, 1 H, bridgehead), 2.2–2.4 (m, 1 H, bridgehead), 0.6–2.2 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 47.0, 43.6, 36.1, 30.4, 28.0, 26.0, 24.9, 11.9. Anal. Calcd for $C_8H_{11}Cl$: Cl, 24.86. Found: Cl, 24.57.

Cyclopropyl Chloride 4 via Diazomethane with Palladium(II) Catalysis. Diazomethane (3.0 g, 71 mmol, generated from 21.5 g of Diazald[15]) was distilled with ether into olefinic chloride **6** (3.21 g, 25.0 mmol) and palladium(II) acetate[15] (0.050 g) in ether (50 mL) at 0 °C. The final solution (350 mL) was stirred at 25 °C overnight. The solid polymethylene was filtered, and the filtrate was rotary evaporated. Gas chromatography (SE-54, 175 °C) showed a **6**:**4** ratio of 83:17. This material was then treated with diazomethane (3.0 g) by the same method as above but with 0.50 g of palladium(II) acetate. Gas chromatography still showed mostly starting chloride with a **6**:**4** ratio of 68:32.

***endo*-2-Chloro-3-methylenenorbornane (8).** *endo*-2-Chloro-*exo*-3-(iodomethyl)norbornane (**7**, 0.57 g, 4.0 mmol) and potassium *tert*-butoxide (0.67 g, 6.0 mmol) were stirred in dry THF (10 mL, distilled from sodium) under nitrogen at 25 °C for 2 h. Water (50 mL) was added, and the mixture was extracted with pentane (3 × 25 mL). The combined extracts were washed with water (5 × 25 mL), dried with anhydrous magnesium sulfate, and filtered, and the filtrate was rotary evaporated and dried in vacuum to give *endo*-2-chloro-3-methylenenorbornane (**8**) as a yellow oil (0.13 g, 0.91 mmol, 23%). Gas chromatography (QF-1, 101 °C, and SE-54, 100 °C) showed only one compound. Other runs gave more material that was less pure because the starting chloride was not purified. Distillation afforded a better sample: bp 27–38 °C (1.4 mm) or 104–118 °C (59 mm); IR (neat) 3079, 2973, 2874, 1665, 1454, 1308, 1229, 949, 893, 854, 793, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.9–5.1 (m, 2 H, $CH_2{=}C$), 4.4–4.6 (m, 1 H, CHCl), 2.7–2.9 (m, 1 H, bridgehead), 2.3–2.6 (m, 1 H, bridgehead), 1.2–2.2 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 154.8 (s), 106.9 (t), 63.4 (d), 44.9 (d), 44.0 (d), 37.3 (t), 30.3 (t), 21.5 (t); MS (EI, 70 eV, 150 °C), *m/e* (%) 142 (M^+, 17), 107 ($M^+ - Cl$, 47), 91 (59), 79 (100), 77 (39); HRMS calcd for $C_8H_{11}Cl$ 142.0548, found 142.0545. Anal. Calcd for $C_8H_{11}Cl$: Cl, 24.86. Found: Cl, 24.48.

Reaction of Chloro Iodide 7 with Potassium *tert*-Butoxide at Reflux. Chloro iodide **7** (2.85 g, 20.0 mmol) and potassium *tert*-butoxide (3.37 g, 30.0 mmol) were refluxed and stirred overnight in dry THF (50 mL) under nitrogen. Workup was as above for the 25 °C reaction. Gas chromatography (SE-54 at 50, 100, or 200 °C) and ^{1}H NMR studies showed chlorides **5**:**8** in a 43:57 ratio.

Reaction of Chloro Iodide 7 with Potassium *tert*-Butoxide in DMSO. Chloro iodide **7** (1.14 g, 8.00 mmol) and potassium *tert*-butoxide (1.34 g, 12.0 mmol) were stirred in DMSO (10 mL) at 25 °C for 2 h. The reaction was exothermic at the beginning and turned brown in 5 min. Water (100 mL) was added, and the mixture was extracted with ether (4 × 50 mL). The combined ether layers were washed with water (5 × 100 mL), dried with anhydrous magnesium sulfate, and filtered, and the filtrate was rotary evaporated and dried in vacuum. ^{1}H NMR spectroscopy showed a **5**:**8** ratio of 37:63.

2-Chloro-3-methylnorbornene (5). Olefinic chloride **6** (14.2 g, 0.111 mol) was added to dry THF (66 mL) and cooled to −78 °C. *tert*-Butyllithium in pentane (66 mL of 1.7 M, 0.112 mol) was added dropwise over 1 h with stirring under nitrogen. The mixture was stirred an additional 30 min, and methyl iodide (18.86 g, 0.113 mol) was added dropwise (**Caution**! Vigorous reaction!) over 1 h. Stirring at 25 °C for 48 h was followed by dropwise addition of water (250 mL). The layers were separated, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were dried with anhydrous magnesium sulfate and filtered, and the filtrate was rotary evaporated and dried in a vacuum to give a blue-green liquid (9.58 g). Vacuum distillation gave a purer product (6.13 g, 0.043 mol, 39%), though contamination from starting material is difficult to overcome: bp 25–35 °C (1.5 mm); IR (neat) 2960, 2879, 1642, 1474, 1448, 1363, 1309, 1081, 1309, 1081, 1003, 802 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.7–2.9 (m, 2 H, bridgeheads), 1.66 (s, 3 H, CH_3), 0.9–1.9 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 138.0 (s), 130.2 (s), 49.1, 47.4, 46.2, 26.1, 25.6, 11.7. The ^{1}H and ^{13}C NMR spectra were identical with those of a sample prepared in another laboratory.[12]

QF-1-Promoted Isomerism of Chlorides. During various studies of chlorides **5** and **8** it became obvious that these compounds were not stable at high temperature in the presence of one of our standard columns, QF-1. A packed $^1/_4$ in. × 22 ft 15% QF-1 column with a helium flow rate of 75 mL/min gave results summarized in Table I from a starting sample containing a **5**:**8** mixture of 42.7:57.3 as determined from the ^{1}H NMR spectral integration and gas chromatography on a capillary SE-54 column, where no change in percentage is noted from 50 to 200 °C.

Heating the original **5**:**8** mixture at 200 °C for 30 min in a sealed tube and analysis by ^{1}H NMR showed no change in ratio. Finally, when a **5**:**8** mixture (42.7:57.3) is chromatographed through the QF-1 column at 102 °C and the peak corresponding to endo chloride **8** is collected and analyzed by NMR, some new absorptions are observed and are in accord with the structure *exo*-2-chloro-3-methylenenorbornane (**9**). The new peaks show a **9**:**8** exo chloride:endo chloride ratio of 70:30 where no **9** was present beforehand. The new peaks of **9** that are different from **8** are the following: ^{1}H NMR ($CDCl_3$) δ 4.21 (CHCl), 5.12 ($CH_2{=}C$); ^{13}C NMR ($CDCl_3$) δ 109.6, 63.1, 46.3, 44.8, 36.0, 29.0, 26.0.

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[14] Alfa Products, Danvers, MA.

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