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Stereoselectivity in the Addition of Dihalocarbenes to 4-*tert*-Butylmethylenecyclohexane and 4-*tert*-Butyl(dichloromethylene)cyclohexane[1]

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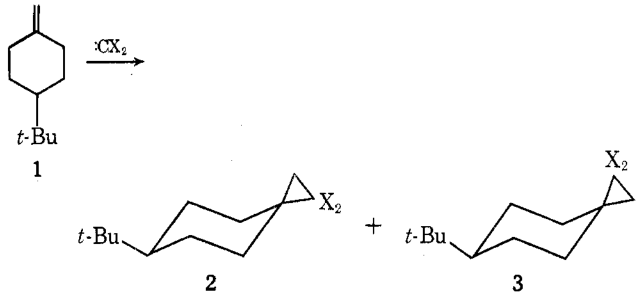
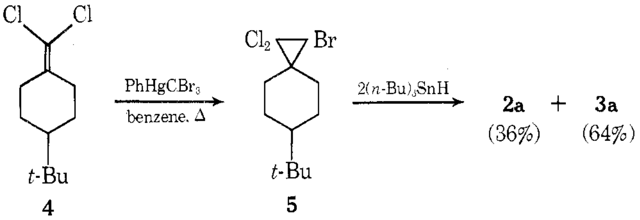
The attack of dichlorocarbene or dibromocarbene on 4-*tert*-butylmethylenecyclohexane (1) produced 80–100% of *E* adduct **2a** resulting from exclusive or predominant equatorial attack. However, the addition of dibromocarbene to 4-*tert*-butyl(dichloromethylene)cyclohexane (4) followed by reduction of the bromine atoms produced a mixture of 36% *E* adduct **2a** and 64% *Z* adduct **3a**, indicating that the equatorial to axial preference for attack by $:CBr_2$ on deactivated olefin 4 is substantially less than for attack by $:CCl_2$ on olefin **1**. The relative rate of addition of $:CCl_2$ to methylenecyclohexane vs. olefin 1 was found to be 1.06 ± 0.02 at 25° in pentane.

The recent proposal that electronic factors may be important in determining the relative amount of axial vs. equatorial attack on double bonds exocyclic to a six-membered ring[2] suggested to us that a study of the stereoselectivity of addition of dihalocarbenes to methylenecyclohexanes containing double bonds of very different nucleophilicities would be of interest.[3]



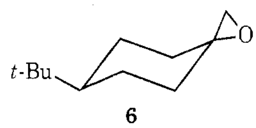
a, X = Cl
b, X = Br

When allowed to react with dichlorocarbene generated by the treatment of ethyl trichloroacetate with sodium methoxide,[4] by the thermal decomposition of sodium trichloroacetate in 1,2-dimethoxyethane,[5] or by the thermal decomposition of phenyl(bromodichloromethyl)mercury in benzene,[6] olefin 1 produced a single, sharp-melting, crystalline product, which exhibits a singlet at τ 8.85 for the cyclopropyl protons in the NMR spectrum. Combustion analysis and spectral data readily confirmed the expected, 1,1-dichloro-6-*tert*-butylspiro[2.5]octane structure. The *E* stereochemistry of spirooctane **2a** was assigned on the basis of a comparison of the NMR spectrum of the compound with that for the corresponding *Z* isomer synthesized by an alternate route (vide infra).



The treatment of dichloro olefin **4** with phenyl(tribromomethyl)mercury followed by reduction of both bromine atoms with tri-*n*-butyltin hydride resulted in a mixture of **2a** and **3a**, crystalline material with a broad melting range. The mixture exhibits two singlets for cyclopropyl protons in the NMR spectrum at τ 8.81 and 8.85, respectively (relative peak areas ca. 1.8:1). It has often been noted that axial methyl and methylene protons on cyclohexane rings absorb at higher field in the NMR spectrum than those which are equatorial.[7–9] For example, the oxymethylene group of oxyspiran **6** absorbs at 0.075 ppm higher field than that of oxyspiran **7**.[8] Therefore the spirooctane with the cyclopropyl methylene absorption at τ 8.85 was assigned structure **2a** while that with the methylene absorption at τ 8.81 was assigned structure **3a**.

As a confirmation of these assignments, the tetradeuterated isomer 8 was prepared from the corresponding α-deu-



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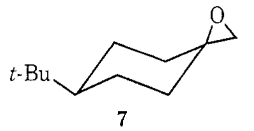

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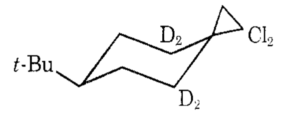

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Table I
Summary of Stereoselectivity Results for Addition of Dihalocarbenes to Olefins 1 and 4

Olefin	Carbene	% of attack Axial	 Equatorial
1	$:CCl_2$	0–20	100–80
1	$:CBr_2$	0–20	100–80
4	$:CBr_2$	36	64

terated ketone by the same synthetic route used to prepare the pure sample of **2a**. A comparison of $W_{1/2}$, the difference in the width at half-height of the cyclopropyl methylene NMR signal and the internal tetramethylsilane signal, between compounds **2a** and **8** showed a 44% decrease for the 90% tetradeuterated isomer **8**. Such a decrease is indicative of the removal of long-range coupling between the axial cyclopropyl protons and the axial cyclohexane protons adjacent to the spiro carbon atom. This phenomenon has been successfully applied to determining the stereochemistry of oxyspiro systems such as **6**.[8]

Because the attack of $:CCl_2$ on olefin **1** and of $:CBr_2$ on deactivated olefin **4** both involve dominant approach from the equatorial direction, we can be confident in assigning the *E* stereochemistry to the single crystalline product isolated from the treatment of olefin **1** with phenyl(tribromomethyl)mercury.

Of special interest is the observed change in the relative amount of axial and equatorial attack as outlined in Table I. That the 4-*tert*-butyl group is not influencing the observed results relative to what might be anticipated for methylenecyclohexane and (dichloromethylene)cyclohexane is suggested by the fact that the relative rate of addition of $:CCl_2$ to methylenecyclohexane vs. olefin **1** was found to be only 1.06 ± 0.02 at 25° in pentane.

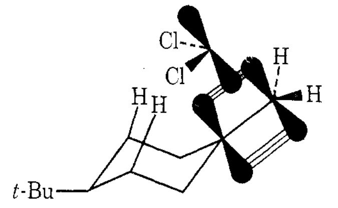
Differences in the stereochemistry of addition of reagents to cyclohexanones were first attributed to the dominance of either "steric approach control" or "product development control".[10] Later workers developed arguments in terms of the relative steric effects of α-axial and β-axial hydrogens toward a group approaching the exocyclic double bond,[11] or in terms of steric vs. torsional factors in the transition state for attack.[12] More recently Klein[2] and Anh[13] have proposed an electronic effect based on the relative size of the π-orbital lobes of the appropriate frontier orbital attacked by a nucleophilic or electrophilic reagent. Their results predict preferential attack by nucleophiles from the axial direction and by electrophiles from the equatorial direction (in the absence of other steric or polar interactions).

Early studies established the electrophilic behavior of $:CCl_2$[14] and $:CBr_2$[15] in additions to olefins. Furthermore, although $:CBr_2$ is recognized to be slightly more reactive (less discriminating) than $:CCl_2$,[14–17] it also exhibits greater steric effects.[14,18,19] The data of Table I show that in spite of the greater steric bulk of $:CBr_2$ relative to $:CCl_2$, reaction of the former intermediate with deactivated olefin **4** resulted in substantially more axial attack than was observed for the reaction of $:CCl_2$ with **1**.

Consider the arguments of Marshall[11a] (and/or Richer[11b]), who suggested that very short distance of the attacking reagent from the exocyclic double bond of a methylenecyclohexane (in the transition state) can be accommodated more readily from the axial than from the equatorial direction, while for long distances the opposite is true. One would indeed expect the transition state for $:CBr_2$ attack on deactivated olefin **4** to be more advanced (shorter divalent carbon to olefin distance) than that for $:CCl_2$ attack on **1**.[17] However, the distance of approach of a reagent to the double bond suggested by the model of Marshall[11a] in order to make axial attack important is less than 2 Å and would represent a product-like transition state,[20] which seems unlikely for the exothermic addition of $:CBr_2$ to **4**.

On the other hand, if we recognize that the electrophilicity of the carbene relative to the nucleophilicity of the olefin is less for the attack of $:CBr_2$ on **4** than for the attack of $:CCl_2$ on **1**, less distinction between axial and equatorial attack preference might be expected for the former reaction based on the electronic arguments outlined by Klein.[2,21]

However, an alternate explanation is possible. Theoretical analysis of the addition of singlet $:CF_2$ to isobutylene[25] indicates a preferred π approach represented by transition states **9** (axial attack) or **10** (equatorial attack) for the addition of $:CCl_2$ to olefin **1**. In each case the p orbital of the divalent carbon is in the same plane occupied by the π-bond of the methylenecyclohexane. (The filled sp^2 orbitals of the carbenes are not shown.) Steric interactions between the chlorines and the β-axial hydrogens in **9** suggest a preference for transition state **10**.



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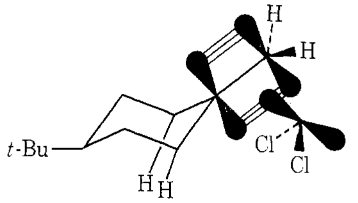

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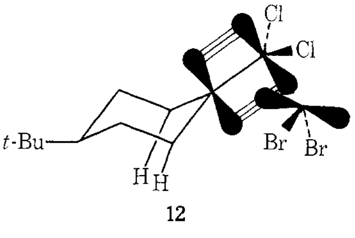
In the reaction of $:CBr_2$ with the deactivated olefin **4** the transition state should be somewhat more advanced than for the addition of $:CCl_2$ to **1**, and the BrCBr plane should be more tilted (as shown in **11** and **12**) toward the orientation it will assume in the product than is the ClCCl plane shown in structures **9** and **10**. If the amount of tilt in the BrCBr plane in **11** relative to that of the ClCCl plane of **9** increases the distance between the halogen and the β-axial hydrogens by more than 0.3 Å, the difference in the sum of the covalent and van der Waals radii for bromine vs. chlorine, the steric interaction in **11** should be less than that in



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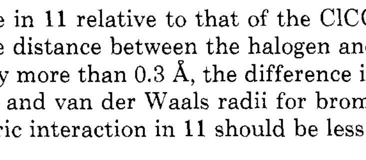

12

9. Because of the large distance between the halogen and the α-axial hydrogens in transition states **10** and **12**, the energy difference should not be very sensitive to changes in the angle of tilt of the XCX plane. Therefore a decrease in the activation energy difference for axial vs. equatorial approach would be expected for attack of $:CBr_2$ on **4** relative to attack of $:CCl_2$ on **1**. Further experimentation to test these concepts is in progress.

Experimental Section

Melting points and boiling points (capillary) are uncorrected. Elemental analyses were performed by the Department of Medicinal Chemistry at the University of Kansas, by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Chemalytics Laboratories, Tempe, Ariz. Ir spectra were obtained from a Beckman IR-8 with a 1604-cm^{-1} (polyester vs. air) reference peak. NMR spectra were obtained on a Varian A-60 or A-60A spectrometer. Mass spectra were obtained on a Varian MAT CH-5 spectrometer.

Phenyl(bromodichloromethyl)mercury, mp 108–110° dec (lit.[26] mp 110–111° dec), was prepared in 73–77% yield by the method of Seyferth and Lambert.[27]

Phenyl(tribromomethyl)mercury, mp 117–119° dec (lit.[27] mp 119–120° dec), was prepared in 60% yield by the above procedure.

4-*tert*-Butylmethylenecyclohexane (1). Sodium hydride (5.04 g, 0.21 mol) was added to dimethyl sulfoxide (140 ml, distilled from CaH_2) and this mixture was stirred at 60° for 6 hr (N_2 blanket) until visible evolution of hydrogen had ceased. Methyltriphenylphosphonium bromide (75 g, 0.21 mol) was added to the cooled mixture (yellow color). After a few mintues 4-*tert*-butylcyclohexanone (38.1 g, 0.25 mol, recrystallized from 95% ethanol, Dow) dissolved in warm dimethyl sulfoxide (40 ml) was added and the mixture was stirred at 60° for several hours. At no time during the reaction was the temperature permitted to go over 75°. The solution was cooled to 25°, water (100 ml) was added, and the product was isolated by extraction with pentane and chromatography of the residue on Florisil (60–100 mesh, 20 g/g of crude product) with petroleum ether (bp 60–110°) as eluent. The first four fractions (100 ml total) were evaporated and the liquid residue was distilled (50-cm wire spiral column) to give **1** (21.5 g, 0.14 mol, 67.3%), bp 70° (10 mm) [lit.[28] bp 185–187° (760 mm)]. Ir and NMR spectra were consistent with those reported.[28]

***(E)*-1,1-Dichloro-6-*tert*-butylspiro[2.5]octane (2a). Parham Method.**[4] Ethyl trichloroacetate (9.57 g, 0.05 mol) was added dropwise (30 min) to a mixture of 4-*tert*-butylmethylenecyclohexane (8.7 g, 0.057 mol), sodium methoxide (3.78 g, 0.07 mol), and pentane (50 ml) cooled in an ice bath, and stirred magnetically for several hours. The reaction mixture was filtered, the filtrate was washed and dried, and the solvent was removed. Olefin, methyl ethyl carbonate, and any remaining ethyl trichloroacetate were removed by fractional vacuum distillation (Nester-Faust autoannular still). Residual yellow solid was recrystallized from absolute ethanol to give white, solid **2a** (3 g, 0.0128 mol, 25.6%): mp 97–97.5°; ir (CS_2) 2900 (s), 2870 (sh), 1430, 1395 (w), 1364, 1272, 1240, 1169 (w), 1138, 1050 (sh), 1040 (cyclopropyl), 1020 (sh), 961, 880, 820 (w), 752 (CCl_2), and 663 cm^{-1}; NMR ($CDCl_3$) broad absorption τ 7.8–8.7 (7 H) and a singlet 8.86 (cyclopropyl CH_2) superimposed on a broad absorption 8.70–9.05 (total 4 H), singlet 9.15 (9 H, *t*-Bu).

Anal. Calcd for $C_{12}H_{20}Cl_2$: C, 61.28; H, 8.57. Found: C, 61.49; H, 8.70.

(An NMR spectrum of the crude product did not reveal the presence of **3a**, although ≤20% could have gone undetected.)

Seyferth Method.[6] Phenyl(bromodichloromethyl)mercury (13.2 g, 0.03 mol), olefin **1** (13.6 g, 0.09 mol), and benzene (35 ml, distilled from CaH_2) were stirred and maintained at reflux for 2 hr. Phenylmercuric bromide (9.8 g, 0.027 mol) was filtered, benzene and excess olefin were evaporated, and the solid residue was recrystallized from ethanol–water to yield **2a** (4 g, 0.017 mol, 56.7%): mp 97–97.5°; ir and NMR spectra were identical with those from product produced by Parham or Wagner methods.

Anal. Calcd for $C_{12}H_{20}Cl_2$: C, 61.28; H, 8.57. Found: C, 61.17; H, 8.40.

Wagner Method.[5] Sodium trichloroacetate (16.69 g, 0.09 mol) was added to a solution of **1** (14.52 g, 0.096 mol) and 1,2-dimethoxyethane (50 ml, freshly distilled from CaH_2), stirred, and kept at reflux overnight. The mixture was filtered, pentane (50 ml) was added to the filtrate, and the resulting solution was washed (saturated NaCl), dried ($MgSO_4$), and evaporated. Distillation of excess olefin (10 mm) from the residue gave **2a** (8.2 g, 0.035 mol, 39%), which was recrystallized from petroleum ether: mp 97–97.5°; ir and NMR spectra were identical with those of the compound produced by the Parham and Seyferth methods. Binary mixtures of this product with that from each of the other generation methods melted sharply at 97–97.5°, as did a ternary mixture. Samples gave a single peak by VPC on 10% OV-210 on 80–100 mesh Gas-Chrom Q (6 ft × 0.125 in. glass).

***(E)*-1,1-Dibromo-6-*tert*-butylspiro[2.5]octane (2b).** Potassium *tert*-butoxide (5.7 g, 0.05 mol), olefin **1** (6.5 g, 0.043 mol), and pentane (50 mol, olefin-free, dry) were combined. Bromoform (10.11 g, 0.04 mol, freshly distilled from CaH_2 and passed through a column of alumina) was added dropwise (30 min) while the mixture was stirred and cooled (ice bath) over a period of 2 hr. The mixture was washed, dried ($MgSO_4$), and evaporated to give a solid which was recrystallized from ethanol–water (4.6 g, 0.142 mol, 35.5%): mp 112–113°; ir (CS_2) 2965 (s), 2870 (sh), 1395 (w), 1365, 1270, 1244 (w), 1167 (w), 1140 (w), 1039, 1019 (sh), 960 (w), 819 (w), 730 (w), and 690 cm^{-1} (s); NMR (CCl_4) broad absorption τ 7.9–9.7 (ca. 7 H), singlet 8.66 (cyclopropyl CH_2) superimposed on a broad absorption 8.7–9.1 (ca. 4 H), singlet 9.13 (9 H, *t*-Bu).

Anal. Calcd for $C_{12}H_{20}Br_2$: C, 44.47; H, 6.22; Br, 49.31. Found: C, 44.60; H, 6.39; Br, 49.19.

1-*tert*-Butyl-4-(dichloromethylene)cyclohexane (4). Dichloromethylenetriphenylphosphorane was prepared by the method of Speziale, Ratts, and Bissing[29] with commercial potassium *tert*-butoxide (11.2 g, 0.1 mol) suspended in a mixture of *tert*-butyl alcohol (7.4 g, 0.1 mol, distilled from CaH_2 and stored over 5-Å molecular sieves) and heptane (300 ml, distilled from CaH_2 and stored over 5-Å molecular sieves). Addition of triphenylphosphine (26.2 g, 0.1 mol) to the cold (0°), stirred slurry (N_2 blanket) followed by dropwise addition (1 hr) of chloroform (11.9 g, 0.1 mol, passed through neutral alumina prior to use) in dry heptane (100 ml) produced the bright yellow Wittig reagent.

After concentration of the solution under vacuum to ca. two-thirds of the original volume, 4-*tert*-butylcyclohexanone (24.0 g, 0.156 mol) was added in 4-g portions (30 min) with the temperature maintained below 10° by an ice bath. Stirring was continued for 2 hr with the ice bath and 5 hr at room temperature. After 48 hr, the reaction mixture was filtered and the filtrate was concentrated on a rotary evaporator with a water bath at 45–50°.

The residue was chromatographed twice on neutral alumina with Skelly B and mixtures of Skelly B with benzene to give crude olefin **4**, which was then recrystallized from petroleum ether to give a small yield of crystalline product (ca. 3 g, 0.014 mol, 9%): mp 53–54.5°; ir (CCl_4) 2970 (s), 2880, 2860, 1618, 1480, 1470, 1440, 1390, 1368, and 1305 cm^{-1} (w) as well as other peaks below 1300 cm^{-1}; NMR ($CDCl_3$) broad doublet τ 6.74 (2 H, J = 13 Hz, 2- and 6-equatorial hydrogens), broad absorptions 7.4–8.23 and 8.23–8.70 (total 7 H), singlet 8.84 (9 H, *t*-Bu); parent ion cluster in mass spectrum (21°, 70 eV) *m/e* (rel intensity) 220 (100), 221 (11.7), 222 (63), 223 (7.5), 224 (10), 225 (1.5); theoretical intensities for $C_{11}H_{18}Cl_2^+$ are 100:12.1:64.8:7.8:10.5:1.3.

Anal. Calcd for $C_{11}H_{18}Cl_2$: C, 59.74; H, 8.20. Found: C, 59.85; H, 8.25.

1,1-Dibromo-2,2-dichloro-6-*tert*-butylspiro[2.5]octane (5). Phenyl(tribromomethyl)mercury (3.05 g, 5.75 mmol) was added to dry benzene (75 ml) followed by olefin **4** (1.11 g, 5 mmol) dissolved in dry benzene (35 ml). The solution was stirred and maintained at reflux (N_2 blanket) for 3 hr and filtered to give phenylmercuric bromide corresponding to >90% decomposition of the starting mercurial. The filtrate was evaporated with the bath temperature at 22° and the solid residue was chromatographed on 25 g of neutral alumina with carbon tetrachloride as eluent. Recrystallization of the crude product from carbon tetrachloride produced colorless crystals (ca. 1.0 g, 2.5 mmol, 50%): mp 138–140°; ir (CCl_4) 2970 (s), 2880, 1470, 1460, 1445, 1390 (w), 1365 cm^{-1} as well as other peaks below 1300 cm^{-1}; NMR ($CDCl_3$) complex multiplet τ 7.95–9.00 (9 H), singlet 9.12 (9 H, *t*-Bu); mass spectrum (54°, 70 eV) parent ion cluster beginning at *m/e* 390 too weak for accurate rel intensity comparison, *m/e* (rel intensity) for $M^+ - CH_3$ are 375 (43), 376 (5.4), 377 (100), 378 (16), 379 (89), 380 (11), 381 (29), 382 (5.4), 383 (5.4); theoretical intensities for $C_{11}H_{15}Cl_2Br_2^+$ are 38.4:4.6:100:12.1:89.5:10.8:31.7:3.8:3.9.

Anal. Calcd for $C_{12}H_{18}Cl_2Br_2$: C, 36.67; H, 4.63. Found: C, 36.85; H, 4.62.

Reduction of 1,1-Dibromo-2,2-dichloro-6-*tert*-butylspiro[2.5]octane. Tri-*n*-butyltin hydride (0.538 g, 1.85 mmol) was added to halospirooctane **5** (0.33 g, 0.84 mmol) and the stoppered reaction vessel was shaken and cooled during the exothermic reaction so as to maintain ca. 25°. After 72 hr at 25°, the reaction mixture was chromatographed on neutral alumina (30 g) with carbon tetrachloride as the eluent. Crude product from the chromatography was recrystallized from absolute ethanol and sublimed to give white, crystalline material (ca. 200 mg, 0.90 mmol, 49%), mp 58–62°, which proved to be a 1.8:1 mixture of *Z* isomer **3**, and *E* isomer **2**: NMR ($CDCl_3$) complex absorption τ 7.95–8.65 (7 H), singlets at 8.81 and 8.85 (cyclopropyl CH_2) superimposed on a broad absorption at 8.65–9.05 (total 4 H, height ratio of downfield to upfield singlet ca. 1.8:1), singlet 9.12 (9 H, *t*-Bu); parent ion cluster in mass spectrum (51°, 70 eV) *m/e* (rel intensity) 234 (100), 235 (14), 236 (65), 237 (9), 238 (12), 239 (2); theoretical intensities for $C_{12}H_{20}Cl_2^+$ are 100:13.2:64.8:8.6:10.5:1.4.

Anal. Calcd for $C_{12}H_{20}Cl_2$: C, 61.27; H, 8.59. Found: C, 61.50; H, 8.43.

2,2,6,6-Tetradeuterio-4-*tert*-butylcyclohexanone. 4-*tert*-Butylcyclohexanone (12.2 g, 0.079 mol), sodium carbonate (0.2 g, 2 mmol), and deuterium oxide (20 ml, 1.0 mol, 99.89% D) were heated and stirred overnight in a tightly stoppered flask at 70° (oil bath). The reaction mixture was extracted with ether, the resulting solution was dried ($CaSO_4$), and the ether was evaporated to give partially deuterated ketone (11.4 g). After three additional exchanges 7 g of deuterated ketone was produced which analyzed for 20.1 atom % excess deuterium,[30] which corresponds to 90.5% deuterium substitution.

2,2,6,6-Tetradeuterio-4-*tert*-butylmethylenecyclohexane. Dimethyl sulfoxide (40 ml) was added to sodium hydride (1.44 g, 60 mmol, obtained from a dispersion in mineral oil, Ventron) followed by the addition (4 min) of methyltriphenylphosphonium bromide (17.8 g, 50 mmol) in warm DMSO (20 ml). Deuterated ketone (7.0 g, 44 mmol) was added rapidly and the reaction mixture was worked up as described for olefin 1 to give tetradeuterated olefin 1 (2.65 g, 15 mmol, 34%), bp 65° (10 mm), slightly contaminated with ketone: ir (CCl_4) 3070 (w), 2950 (s), 2860 (sh), 1650, 1480, 1395 (w), 1365, 1240 (w), 1060 (w), 1010 (w), 916 (w), 885 (s), 730 cm^{-1} (w); NMR (CCl_4) singlet τ 5.49 (2 H, vinyl), broad absorption 7.6–9.0 (5 H), singlet 9.15 (9 H, *t*-Bu).

***(E)*-1,1-Dichloro-4,4,8,8-tetradeuterio-6-*tert*-butylspiro[2.5]octane (8).** Deuterated olefin (1.59 g, 10 mmol) was combined with phenyl(bromodichloromethyl)mercury (4.61 g, 10.5 mmol) in benzene (20 ml) and the reaction and work-up were conducted as previously described for the Seyferth method. Phenylmercuric bromide (3.6 g, 10.1 mmol, 96.2%) was isolated. Product **8**, was recrystallized from ethanol (1.20 g, 5 mmol, 50%): ir (CS_2) virtually identical with that of protiated compound **2a**; NMR (CCl_4) showed expected diminution of cyclohexane signal. The product analyzed for 16.6 atom % excess deuterium,[30] which corresponds to 83% deuterium substitution.

Measurement of NMR Half Band Widths. Compounds **2a** (0.0719 g) and **8** (0.0903 g) were dissolved separately in sufficient carbon tetrachloride containing Me_4Si (2.5% by volume) that the cyclopropyl peak and the Me_4Si peak were approximately equal in height. A few drops of benzene (spectral grade) were added to each sample to provide a lock for the 100-MHz spectrometer. Spectra were obtained twice from both a Varian HA-100 and a Varian A-60A spectrometer each time. In each case a 50-cycle sweep width, a sweep time of 0.5 Hz, a filter band width of 4, and a radiofrequency field setting of 0.1 were employed.

The cyclopropyl proton peak was swept repeatedly, the width at half-height was measured to the nearest 0.01 Hz for each sweep, and these sweep widths were averaged for the peak. The sweep offset was adjusted to bring the Me_4Si peak on scale and a similar series of sweeps were made, half-height widths measured, and an average obtained for the Me_4Si proton peak in the same sample. The difference between sample and Me_4Si peak widths, rather than an absolute measurement of the sample peak width, was employed to minimize random variations in spectrometer sensitivity between spectra.[8]

The average value for $\Delta W_{1/2}$ for the cyclopropyl CH_2 of spiran **2a** was 0.70 ± 0.13 Hz, while that for tetradeuterated spiran **8** was 0.39 ± 0.05 Hz.

Competitive Addition of Dichlorocarbene to Methylenecyclohexane and Olefin 1. Methylenecyclohexane (2.40 g, 25 mmol) and olefin 1 (3.80 g, 25 mmol) were dissolved in 5 ml of olefin-free pentane (stored over Na wire). This solution was added to a suspension of sodium methoxide (0.81 g, 15 mmol) in pentane (5 ml). Ethyl trichloroacetate (0.952 g, 5 mmol) was added dropwise and the mixture was stirred at 25° for 1.5 hr after all the ester had been added. The reaction mixture was filtered and the residue was rinsed with pentane. Combined pentane solutions were dried ($CaSO_4$) and evaporated for 10 min under aspirator vacuum with no external heating.

Aliquots were analyzed on 10% OV-210 (80–100 mesh Gas-Chrom Q, 6 ft × 0.125 in. glass column). The average value (several injections) for the ratio *k*(methylenecyclohexane)/*k*(4-*tert*-butylmethylenecyclohexane) corrected by a detector sensitivity factor was 1.06 ± 0.02.

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Registry No.—**1**, 13294-73-0; **1**-2,2,6,6-d_4, 54789-06-9; **2a**, 54789-07-0; **2b**, 54789-08-1; **3a**, 54831-18-4; **4**, 54789-09-2; **5**, 54789-10-5; **8**, 54831-19-5; dichlorocarbene, 1605-72-7; dibromocarbene, 4371-77-1; 4-*tert*-butylcyclohexanone, 98-53-3; ethyl trichloroacetate, 515-84-4; phenyl(bromodichloromethyl)mercury, 3294-58-4; sodium trichloroacetate, 650-51-1; dichloromethylenetriphenylphosphorane, 6779-08-4; phenyl(tribromomethyl)mercury, 3294-60-8.

References and Notes

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