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Dihalocarbene Insertion Reactions into C−H Bonds of Compounds Containing Small Rings: Mechanisms and Regio- and Stereoselectivities†,‡

Udo H. Brinker,*,§,|| Guoying Lin,|| Linxiao Xu,|| William B. Smith,⊥ and Jean-Luc Mieusset§

Institut für Organische Chemie, Universität Wien, Währinger Str. 38, 1090 Wien, Austria, Department of Chemistry, State University of New York at Binghamton, New York 13902-6016, and Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Udo.Brinker@univie.ac.at

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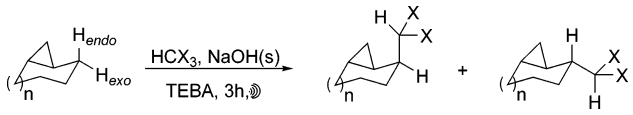

Novel insertion reactions of dichloro- and dibromocarbene into carbon−hydrogen bonds adjacent to cyclopropane rings are reported. It is found that the predominant isomers formed in the reactions with bicyclo[4.1.0]heptane result from insertion into the *endo* carbon−hydrogen bonds alpha to the three-membered ring. In the reactions of bicyclo[3.1.0]hexane, however, the *exo* dihalocarbene insertion products are formed as the major isomers. In some compounds cyclopropane rings "activate" adjacent carbon−hydrogen bonds, whereas other systems containing three-membered rings do not. Moreover, the influence of various substituents (methyl, geminal dimethyl, phenyl, methoxy, and ethoxy) attached to bicyclo-[3.1.0]hexane and bicyclo[4.1.0]heptane in dihalocarbene reactions has been studied. The findings can be explained by the concept of maximum orbital overlaps of Walsh orbitals of the cyclopropane rings and the α carbon−hydrogen bonds. In stark contrast, selective insertion into the tertiary carbon−hydrogen bonds of the cyclobutane ring in bicyclo[4.2.0]octane is observed.

Introduction

Earlier on we reported that dichloro- and dibromocarbenes can stereoselectively insert into the C−H bonds located at the α positions to three-membered rings.[1] Now we wish to elaborate on this peculiar dihalocarbene reaction behavior, which can lead to the functionalization of hydrocarbons containing three-membered rings.

It was discovered over 40 years ago[2] that dihalocarbenes can insert into carbon−hydrogen bonds. Since then, several different C−H bond insertion reactions of dihalocarbenes have been revealed.[3] A dihalocarbene can insert into a C−H bond that has been activated by the presence of an adjacent heteroatom: oxygen,[4−13] nitrogen,[14] or sulfur.[2] In addition, activation using compounds containing π bonds, such as vinyl,[15−17] carbonyl,[18] and phenyl[6−8,15b,19] moieties has also been studied.

† This paper is dedicated to Prof. E. Vogel on the occasion of his 80th birthday.

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* Corresponding author. Phone: +43−1−4277−52121. Fax: + 43−1−4277−52140.

§ Universität Wien.

|| State University of New York at Binghamton.

⊥ Texas Christian University.

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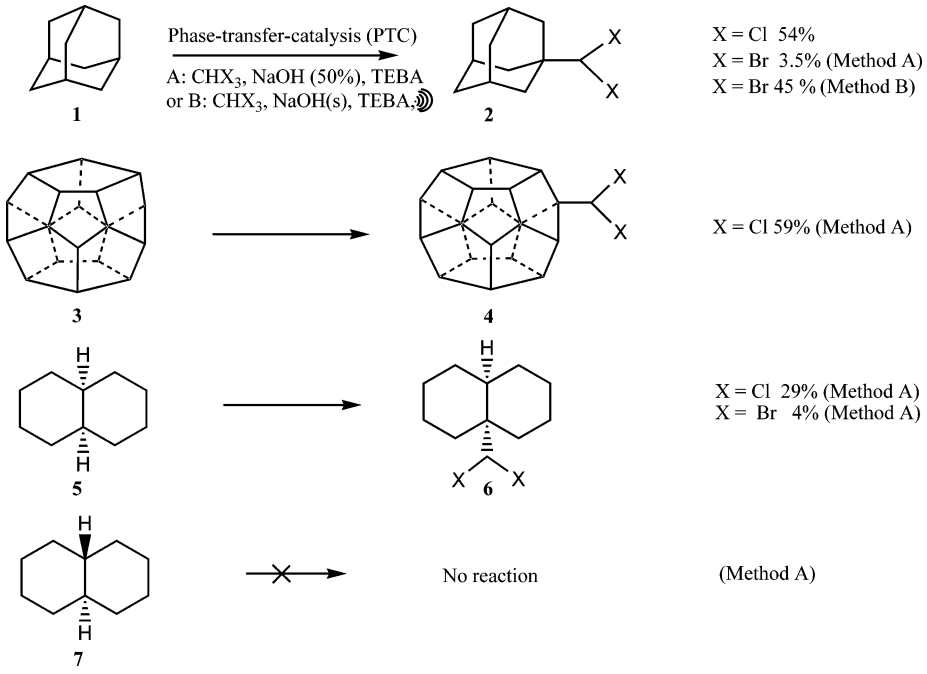

FIGURE 1. Reaction of dihalocarbenes with some hydrocarbons.

In contrast, intermolecular insertions of dihalocarbenes into nonactivated C−H bonds succeeded only with spheroidal molecules such as adamantane (**1**)[20,21] and dodecahedrane (**3**),[22] where insertion exclusively occurred at the tertiary C−H bonds (Figure 1). Moreover, insertion reactions of dichlorocarbene with a number of polycyclic hydrocarbons have been studied.[23] For example, it was found that use of the ultrasonication method[1] for the generation of dibromocarbene increased the yield of insertion product **2** from 3.5% to 45%. Other saturated hydrocarbons ordinarily afford only very low yields[6,8,15] or do not react at all. For instance, the reaction of *cis*-decalin (**5**) with dibromo- and dichlorocarbene gave only low yields of insertion products **6**, and *trans*-decalin (**7**) proved to be inert.[6,8]

It is a generally held belief that the insertion of carbenes into covalent bonds is the most characteristic reaction of free divalent carbon species.[3]

The insertion can be envisioned as occurring by one or more of three possible general mechanisms:[24] (a) a concerted, or direct insertion by way of a triangular activated complex, (b) a stepwise abstraction-recombination involving a radical or ion-pair intermediate, and (c) coordination to form an ylide, followed by rearrangement (Figure 2). Singlet carbenes may be capable of reacting by any of these mechanisms, though mechanism b would involve an ionic rather than a radical pair intermediate and mechanism c would be restricted to the reaction of the carbene with molecules containing lone-pair electrons. Triplet carbenes should favor mechanism b with intermediate formation of a radical pair, which collapses to give the formal insertion product.

Dihalocarbenes are widely used in synthetic organic chemistry and provide unique methods in some cases. They can be generated in a number of different ways. Phase transfer catalysis (PTC) is the most convenient method.[3d,6,7] Furthermore, different procedures for their generation produce dihalocarbenes with different reactivities. For example, dihalocarbenes resulting from the decomposition of Seyferth's trihalomethylphenylmercury reagents also can insert into β C−H bonds of organomercury,[25] -silicon,[26−28] -germanium,[29] and -tin[26] compounds.

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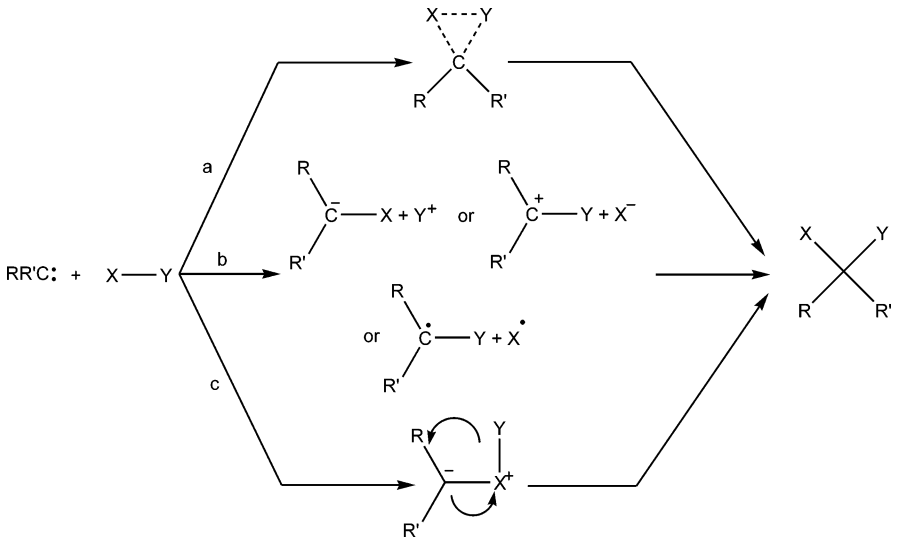
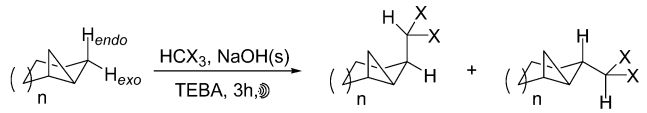


FIGURE 2. Carbene insertion mechanisms.



n = 1	**8**	X = Cl	**9a**	**9b**
		X = Br	**10a**	**10b**
n = 0	**11**	X = Cl	**12a**	**12b**
		X = Br	**13a**	**13b**

FIGURE 3. Reactions of bicyclo[4.1.0]heptane (**8**) and bicyclo[3.1.0]-hexane (**11**) with dichloro- and dibromocarbene.

"Saturated hydrocarbons are among the most ubiquitous, and chemically stable, of all organic materials."[30] They appear in petroleum, in coal, in synthetic fuels produced by liquefaction of coal and other fossil fuels, and in synthetic fuels produced by Fischer−Tropsch chemistry from syngas. It is one of the most intriguing and yet elusive goals in chemistry to "activate" carbon−hydrogen bonds in completely saturated organic compounds.

The activation of saturated hydrocarbons[31] is described as chemists' "Holy Grail",[32] because of the exciting possibilities. For example, if a dihalomethyl group could be introduced into a molecule such as bicyclo[4.1.0]heptane (norcarane) (**8**)[33] (Figure 3) and then hydrolyzed into an aldehyde group, the whole molecule would be functionalized.

Molecules such as adamantane (**1**) and dodecahedrane (**3**) consist of five- and six-membered rings, and they react with dichlorocarbene quite readily, affording good to moderate yields of insertion products (Figure 1). In contrast, bicyclo[4.1.0]-heptane (**8**)[33] (Figure 3) comprises one six- and one three-membered ring. Will the presence of the electron-rich three-membered ring, and its specially oriented Walsh orbitals in **8**, have an effect when the molecule is attacked by an electrophilic dihalocarbene in insertion reactions? Will the molecule react differently from those molecules which consist only of five- and six-membered rings?

Although reactions of dihalocarbenes with bicyclo[1.1.0]-butane derivatives and other strained compounds containing three-membered rings have been studied for about 40 years,[34,35] C−H bond insertion reactions of dihalocarbenes with hydrocarbons containing three- or four-membered rings have not been reported. We reasoned that selective insertion into C−H bonds α to a three-membered ring would occur, if the Walsh orbitals of the cyclopropane ring and suitable C−H orbitals interact.

Results

The chemical[36] and biological[37] effects of ultrasound were first reported about 80 years ago. Ultrasound utilization in organic synthesis, however, has been broadly applied only in the last 15 years.[38,39] Ultrasound waves can affect PTC-catalyzed reactions, dramatically increasing yield and purity.[39] Under

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(35) When investigating reactions of bicyclo[2.1.0]pentane with dicarbomethoxycarbene and phenylcarbene generated by photolysis of the corresponding diazo precursors, Jones, et al. found *exo*:*endo* isomers resulting from C−H insertions (ratio ca. 1:2.7 and 1:2.4, respectively). With difluorocarbene, however, no C−H insertion product was found. See: Shiue, G.-H.; Misslitz, U.; Ding, X.; Jones, M., Jr.; de Meijere, A. *Tetrahedron Lett.* **1985**, *26*, 5399.

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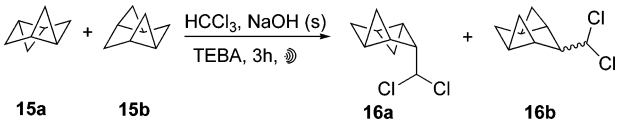

FIGURE 4. Reactions of tricyclic octanes with dichlorocarbene.

ultrasonication use of chloroform and powdered NaOH, a solid−liquid two-phase system, usually affords high yields of dihalocarbene adducts with alkenes.[40,41]

When a mixture of bicyclo[4.1.0]heptane (**8**), chloroform, powdered sodium hydroxide, and 0.5% of triethylbenzylammonium chloride (TEBA) was ultrasonicated in the water bath of an ultrasonic cleaner (35 kHz, 120 W) for 3 h, 2-(dichloromethyl)-bicyclo[4.1.0]heptane (*endo* **9a**) and (*exo* **9b**) were obtained in a yield of 83% (ratio = 4:1).[1] As determined by NOE experiments, the dichloromethyl group in the major isomer **9a** is located at the *endo* position. No product resulting from insertion of dichlorocarbene into the tertiary C−H bonds was found.[1]

With bicyclo[4.1.0]heptane (**8**), no reaction took place when dichlorocarbene generated by the Doering−Hoffmann method[33a] ($HCCl_3$, *t*-BuOK) was used. However, under normal PTC conditions[3d] ($HCCl_3$, 50% aq. NaOH, 5% TEBA, 9 h), a 15% yield of **9a** and **9b** was obtained (ratio: ca. 4:1).[1] When bromoform in dichloromethane was used,[41b] the C−H insertion products **10a** and **10b** were formed in 27% yield. Thus, dichloro- and dibromocarbene insert selectively into the C−H bonds adjacent to the three-membered ring of **8**.[1]

Similarly, dichlorocarbene insertion into the C−H bonds at C2 or C4 of bicyclo[3.1.0]hexane (**11**)[42] afforded **12a** and **12b** in 40% yield. The *exo* product **12b** is favored in this reaction (*endo*:*exo* = 1:3).[1] This is a completely opposite stereochemical outcome when compared with the :CCl_2 insertion with **8** (*endo*:*exo* = 4:1)! In the corresponding dibromocarbene insertion reaction with **11**, compounds **13a** and **13b** were formed in a ratio of 1:4.

The insertion reactions of dichlorocarbene with **15a**[43] and **15b**[44] (ratio = 7:1) yielded 57% of **16a** and **16b** (Figure 4). The *syn* isomer **15b** was found to be more reactive than the *anti* isomer **15a** by gas chromatographic monitoring of the reaction progress. Like the formation of the *endo* isomer **9a** in the reaction with **8**, the insertion reaction with **15b** leads to the formation of *endo* **16b** as the major isomer. In addition to **16a** and **16b**, as indicated by ^1H, ^{13}C NMR, and GC-MS, five bis-insertion products were detected. These products clearly derive from one C−H insertion each at positions C2 and C5: (1) *syn* bis-insertion of **15a**, (2) *anti* bis-insertion of **15a**, (3) *endo syn* bis-insertion of **15b**, (4) *exo syn* bis-insertion of **15b**, and (5) *anti* bis-insertion of **15b**.

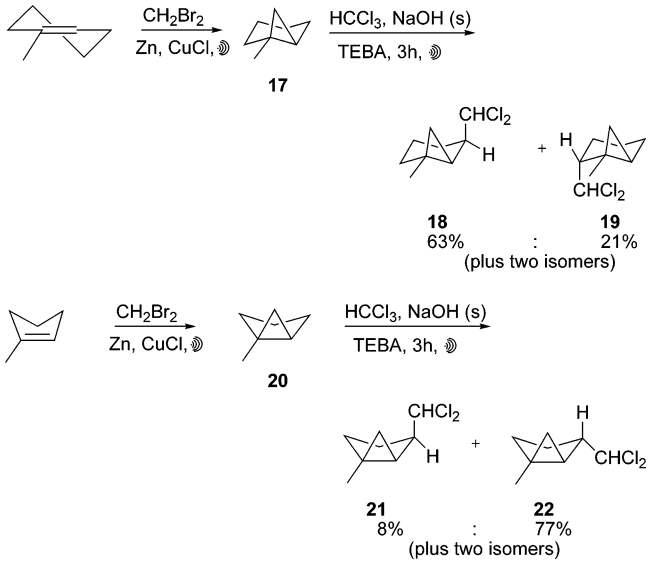

FIGURE 5. Synthesis of 1-methylsubstituted bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane and their reaction with dichlorocarbene.

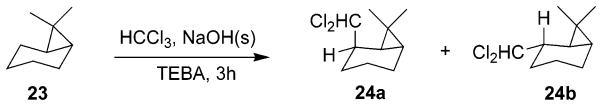

FIGURE 6. Reaction of 7,7-dimethylbicyclo[4.1.0]heptane with dichlorocarbene.

When 1-methylbicyclo[4.1.0]heptane (**17**)[45] was reacted with dichlorocarbene, **18** was isolated as the major product containing the dichloromethyl group at C5 in *endo* position to the three-membered ring (Figure 5).

1-Methylbicyclo[3.1.0]hexane (**20**),[45] however, yielded **22** as the major product containing the dichloromethyl group at C4 in *exo* position. The stereochemical result of this reaction, therefore, is in accord with the parent compound **11**.

When 7,7-dimethylbicyclo[4.1.0]heptane (**23**),[46] in which the *geminal* dimethyl groups impose steric hindrance for *endo* attack at C2 and C5, was reacted with dichlorocarbene, insertion products similar to those obtained with the parent compound **8** were observed in a yield of 55% (Figure 6).

However, the *endo*:*exo* ratio of products dropped from 4:1 (**9a**:**9b**) to 1.13:1 (**24a**:**24b**), favoring only slightly the insertion at the *endo* position.

It is well-known, that dihalocarbenes can insert into C−H bonds α to heteroatoms (vide supra). Introduction of a methoxy group into bicyclo[3.1.0]hexane and the norcarane system at C1 should change the electron density distributions in **25** and **26**, making them much different from that of the parent system **11** and **8**, respectively. Due to the proximity of the oxygen atom to the C−H bonds at C2 in **25** and **26**, it was speculated that the insertion of an electrophilic dichlorocarbene would be rerouted more to the *exo* position, because of its attraction to the lone-pair electrons on oxygen. However, when 1-methox-

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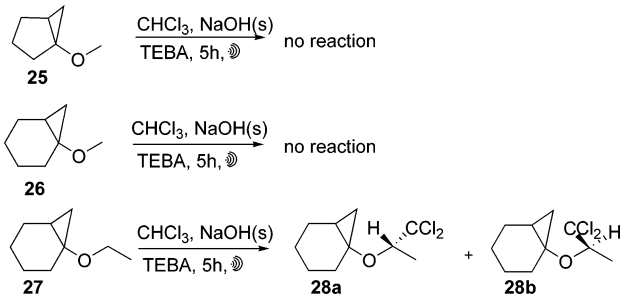

FIGURE 7. Reactions of bicyclic ethers with dichlorocarbene.

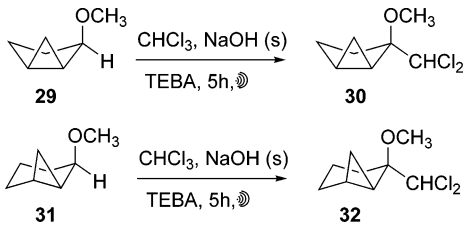

FIGURE 8. Reactions of 2-methoxy-substituted bicyclic compounds with dichlorocarbene.

ynorcarane (**25**)[47] was treated under standard conditions, there was no reaction (Figure 7). Neither products deriving from insertion into the primary C−H bonds of the methyl group nor products resulting from insertion into any other C−H bonds were observed. Not surprisingly, when 1-methoxybicyclo[3.1.0]-hexane (**26**)[47] was treated with dichlorocarbene, it did not react either. 1-Ethoxynorcarane (**27**),[47,48] however, reacted with dichlorocarbene to give a 47% yield of the insertion products **28a** and **28b**, which derive from dichlorocarbene insertion into the α C−H bonds of the ethoxy group.

The introduction of *endo* methoxy groups at C2 should lead to insertion of dichlorocarbene into the *tertiary* C−H bonds of 2-*endo*-methoxybicyclo[3.1.0]hexane (**29**)[49] and 2-*endo*-methoxybicyclo[4.1.0]heptane (**31**) (Figure 8).[49]

These bonds are activated by the oxygen atom and are in the α position to the three-membered ring. Indeed, in the reaction with dichlorocarbene, **29** and **31** produced exclusively **30** and **32** in yields of 94% and 96%, respectively.

When 1-phenylbicyclo[4.1.0]heptane (**33**)[45a,50] was reacted with dichlorocarbene, the reaction proceeded only very slowly, affording a mixture of the four insertion products **34**, **35**, and **36** in a total yield of 30% (Figure 9). All products formed contained the dichloromethyl group either at C5 (65%) or at C2 (35%).

NOE experiments confirmed the stereochemistry of the major isomer **34**. When C7−H_{endo} was irradiated, the methine proton

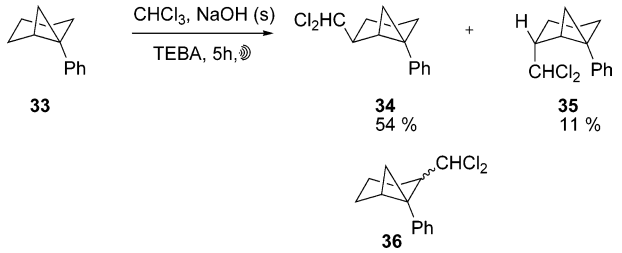

FIGURE 9. Reaction of 1-phenylbicyclo[4.1.0]heptane with dichlorocarbene.

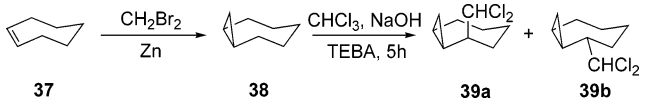

FIGURE 10. Reaction of bicyclo[5.1.0]octane with dichlorocarbene.

of the dichloromethyl group at C-5 showed 5% enhancement. And vice versa, when the methine proton on the dichloromethyl group was irradiated, an enhancement of the signal assigned to C7−H_{endo} was observed.

The effect of the three-membered ring toward activation of α C−H bonds in compounds containing the bicyclo[3.1.0]-hexane and bicyclo[4.1.0]heptane skeleton, respectively, has been shown above.

Does this also apply to the higher homolog, i.e., bicyclo-[5.1.0]octane (**38**),[51] containing a seven-membered ring? Since the seven-membered ring in **38** is more flexible than the six-membered ring in norcarane **8**, in its derivatives **17**, **23**, **26**, **27**, and **33**, and in the bicyclo[3.1.0]hexane systems **11**, **20**, **25**, and **29**, the insertion of dichlorocarbene might take a different course. To explore this idea, **38** was first synthesized from cycloheptene according to the literature (Figure 10).[45] The reaction of **38** with dichlorocarbene, generated by ultrasonication, resulted in products **39a** and **39b** in a ratio of 2.4:1 (yield: 65%). NOE effects between the dichloromethyl group and the *endo* C−H at C8 showed that in the major compound **39a** the three-membered ring and the dichloromethyl group are in an *endo* relationship.

Compounds **39a** and **39b**, interestingly, show almost identical chemical shifts for the dichloromethyl group at δ 5.92 ppm and δ 5.91 ppm, respectively. Also, the coupling constants J_2, 3.3 and 2.7 Hz, respectively, differ only slightly (vide infra).

Activation caused by a three-membered ring should be less pronounced in conformationally rigid polycyclic ring systems. Due to freedom of rotation of the side chains, this should also be true for compounds comprising alkyl groups attached to the cyclopropane unit.

An example is *cis*-1,2-diethylcyclopropane (**41**)[52] (Figure 11) which is much less conformationally restrained than norcarane **8** and some of its derivatives, such as **17**, **23**, **26**, **27**, and **33**. If orbital overlapping does play an important role in determining the stereochemistry of the insertion products, **41** should react with dichlorocarbene differently than norcarane **8**.

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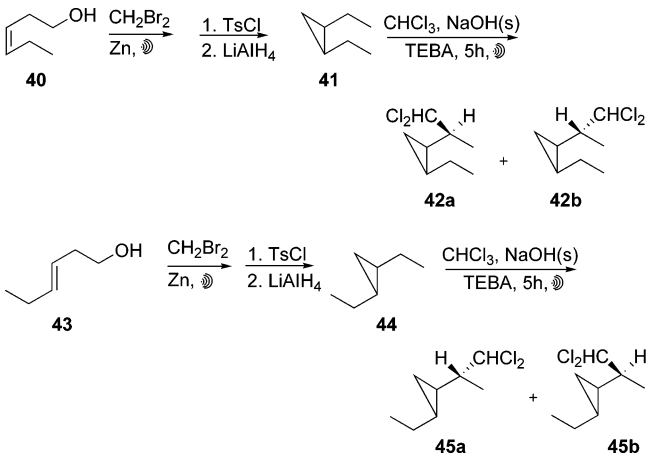

FIGURE 11. Synthesis of *cis*- and *trans*-1,2-diethylcyclopropane and their reactions with dichlorocarbene.

cis-1,2-Diethylcyclopropane (**41**)[52a,b] was prepared starting from **40**. Cyclopropanation, followed by tosylation of the hydroxyl group, and reduction with $LiAlH_4$ afforded **41** in an overall yield of 47%. When *cis*-1,2-diethylcyclopropane (**41**) was reacted with dichlorocarbene, the two insertion products **42a** and **42b** were obtained in a yield of 30%. In addition, the starting material was recovered. The ^{1}H NMR spectrum of the product mixture clearly showed the presence of two isomers in a ratio of 3:2. Since the downfield doublets ($\delta = 5.92$ and 5.91) for the $CHCl_2$ groups both displayed nearly the same coupling constants (vide infra), it is difficult to assign the stereochemistry for **42a** and **42b**. Nevertheless, this result shows that dichlorocarbene still has a preference for the four C−H bonds in the α position to the three-membered ring. The lower yield of **42a** and **42b** in comparison to the yields of **9a** and **9b** obtained from the reaction with norcarane **8** might result from a less favorable interaction of the orbitals in the less restrained ethyl chains in **41**. An attempt to improve the yield of **42a** and **42b** by performing the reaction in a pressure bottle resulted in a violent explosion.[53]

trans-1,2-Diethylcyclopropane (**44**)[52a,52c] was synthesized in the same fashion as **41**. When **44** was allowed to react with dichlorocarbene under the same conditions as **41**, compounds **45a** and **45b** were obtained in a total yield of 29%. The ^{1}H NMR spectrum of the crude mixture showed only two products in a ratio of 1.3:1. After separation by preparative gas chromatography (PGC), **45a** and **45b** were isolated. The stereochemistry of these compounds, however, is unknown.

It is interesting to note that the reaction of dichlorocarbene with spiro[2.5]octane (**46**)[54] (Figure 12), gave only ca. 2% insertion products, whereas 1-methyl-1-phenylcyclopropane (**47**)[55] did not react at all under ultrasonication.

We have shown that some compounds containing properly positioned cyclopropane rings are attacked by dihalocarbenes regioselectively and stereospecifically at their C−H bonds α to the cyclopropane ring. Our next endeavor was to establish whether cyclopropane's homolog, cyclobutane, would affect the C−H insertion reactions of dihalocarbenes in a similar fashion.

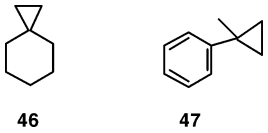

FIGURE 12. Spiro[2.5]octane and 1-methyl-1-phenylcyclopropane.

cis-Bicyclo[4.2.0]octane (**52**) was synthesized from *cis*-anhydride (**48**)[56] according to the literature (Figure 13). Reduction to **49**, followed by tosylation, gave **50**. Preparation of the diiodide **51** and ring closure afforded *cis*-bicyclo[4.2.0]octane (**52**) in an overall yield of 84%.

In stark contrast to the reaction with norcarane **8**, reaction with **52** resulted in the insertion of dichlorocarbene at the *tertiary* C−H bonds at the bridgehead position to afford **53** in a yield of 90%. No products resulting from insertion into C−H bonds adjacent to the cyclobutane ring were found!

The high yield of **53** observed in the reaction of **52** with dichlorocarbene encouraged us to synthesize the corresponding *trans*-bicyclo[4.2.0]octane (**57**)[56a] which contains *tertiary* C−H bonds barred by the four- and six-membered rings (Figure 14).

The *tertiary* C−H bonds in this molecule should be much less accessible than those in the corresponding *cis* compound.

The synthesis of **57**[56a] was accomplished according to the literature with minor variations. Reduction of **54** afforded diol **55** in a yield of 90%. Diiodide **56**[57] was prepared from **55** in 75% yield. The ring closure to **57** was achieved in a yield of 90%, using ultrasonication. As has been shown earlier in the dichlorocarbene insertion reaction of decalin,[6,8] the bridgehead C−H bonds of the *cis* isomer **5** can receive insertion with a moderate yield, whereas the *trans* isomer **7** does not react at all. Not surprisingly, when *trans*-bicyclo[4.2.0]octane (**57**) was allowed to react with dichlorocarbene, no reaction took place (see Figure 1). Obviously, the bridgehead C−H bonds in **7** and **57** are well enough hidden between the two carbocyclic rings and are spatially not accessible. In contrast, the *tertiary* bridgehead C−H bonds are standing out in molecules such as adamantane (**1**), dodecahedrane (**3**), and *cis*-bicyclo[4.2.0]octane (**52**) and, therefore, can receive insertions of carbenes.

Discussion

Theoretical Aspects of Carbene Insertion Reactions. Insertion reactions of carbenes into C−H bonds have been broadly treated in the realm of theory.[58] A representative case was an application of extended Hückel molecular orbital theory by Hoffmann et al.[59] in 1971. They reported that carbenes prefer to approach the hydrogen atom of a C−H bond in the so-called end-on mechanism (Figure 15). In this mechanism, the vacant p orbital of the carbene attacks the target hydrogen atom. Hoffmann's calculations were supported by Dewar at the MINDO/2 level.[60]

(53) Caution: A good refluxing condensor is recommended. When a pressure bottle was used, it resulted in a violent explosion.

(54) Shortridge, R. W.; Craig, R. A.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1948**, *70*, 946.

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(56) (a) Samuel, C. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1259. (b) Bailey, W. F.; Gagnier, R. P. *Tetrahedron Lett.* **1982**, *23*, 5123. (c) Brinker, U. H.; König, L. *Chem. Lett.* **1984**, 45.

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(59) Dobson, R. C.; Hayes, D. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6188.

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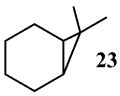
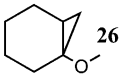
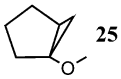
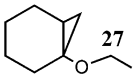
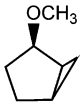
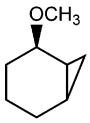
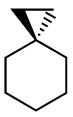
TABLE 1. Insertion Reactions of :CX_2 into C−H Bonds

compounds	products (ratio, %)[a]	yield (%)[b]
 **11**	*endo* *exo* Cl 26 74 Br 20 80	40 18
 **8**	*endo* *exo* Cl 81 19 Br 80 20	83 (15)[c] 27
 **38**	*endo* *exo* 71 29	65
 **20**	4-*endo* 4-*exo* other 8 77 15	36
 **17**	5-*endo* 2-*exo* other 63 21 16	83
 **33**	5-*endo* 5-*exo* other 54 11 35	30
 **23**	*endo* *exo* 53 47	55
 **26**	no reaction	0
 **25**	no reaction	0
 **27**	55 45	47[d]
 **29**	2-*exo* 100	93[e]
 **31**	2-*exo* 100	96[e]
 **41**	60 40	29
 **44**	56 44	30
 **46**	three isomers[f]	2
		trace

[a] Relative ratios measured by ^{1}H NMR spectroscopy. [b] Total yields. [c] 50% NaOH, $CHCl_3$, 15 h. [d] Insertion occurred into the secondary C−H bonds in the ethoxy group. [e] Exclusively 2-*exo* insertion. [f] Ratios = 5:1:1 based on ^{1}H NMR signals of $CHCl_2$ groups.

However, many experimental results disagree with the end-on mechanism.[61] It should especially be noted that, in intramolecular reactions, the perpendicular attack is favored, whereas the end-on approach is often sterically impossible. For example, in reaction **58** → **59** (Figure 16), it has been shown experimentally that the resulting carbene inserted specifically into the *exo* C(3)−H bond of the bicyclo[2.2.1]heptane system to give the highly strained **59**.[61] However, it is worth noticing that preliminary DFT calculations disagree with this result. They predict that the insertions into *endo* C(3)−H, *endo* C(5)−H, and *endo* C(6)−H bond are strongly preferred over insertion into *exo* C(3)−H.

Moreover, at the levels of theoretical calculations previously mentioned, too many parameters had not been optimized. Other theoreticians later analyzed the methylene insertion reaction into C−H bonds at the more sophisticated ab initio level.[62,63] When third-order Møller-Plesset perturbation theory corrections were included (MP3/6-31G*/HF/3-21G), barriers for the :CH_2 insertion into methane and ethane were calculated to be 0 and 0.2 kcal/mol, [62b−d] respectively. At the level of MP4/6-31G*// MP2/6-31G, QCISD/6-31G*// QCISD(T)/6-31G*, and QCISD-(T)/6-311+G(2df,p)//QCISD(T)/6-31G*, the barriers for the :CH_2 insertion into methane are zero and even of negative value; it is therefore a barrierless process.[63c] Two approaches, the π and the σ approach (Figure 17), were considered.[63c,e]

In this calculation, each produced almost the same result. In the transition state of the insertion, the empty p orbital of the carbene approaches the σ bond of the C−H bond to be attacked. When the distance between the carbene carbon and the carbon of the C−H bond reaches 2.135 Å, at the level of QCISD/6-31-G*, the hydrogen of the C−H bond moves to the bigger lobe of the σ sp^2 orbital of the former divalent carbon.

Mechanisms for Insertion Reactions of Dihalocarbenes. Previous research in this area has shed some light on carbene insertion reaction mechanisms. In reactions with ether, dichlorocarbene insertion into C−H bonds α to the oxygen atom is highly favored over insertion into the C−H bonds of the methylene group.[33b] Isobutyl methyl ether, with a *tertiary* C−H bond β to the oxygen and a secondary C−H bond α to the oxygen, gave $Me_2CHCH(CCl_2H)OMe$ as the major product in the reaction with $PhHgCCl_2Br$.[5c] Tetrahydrofuran, with secondary C−H bonds both in α and β positions to the oxygen atom, underwent insertion only at the α position.[4a,4b,5a,5c,7] An isolated terminal C−C double bond is much more reactive than a C−H bond adjacent to a methoxy group. For example, with CH_2═$CHCH_2CH_2OCH_3$, only the expected *gem*-dihalocyclo-

(61) Gutsche, C. D.; Bachman, G. L.; Udell, W.; Bäuerlein, S. *J. Am. Chem. Soc.* **1971**, *93*, 5172.

(62) (a) Raghavachri, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5853. (b) Raghavachri, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5421. (c) Gordon, M. S.; Boatz, J. A.; Gano, D. R.; Friederich, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 1323. (d) Cremaschi, P.; Simonetta, M. *J. Chem. Soc. Faraday Trans. II* **1974**, 1801. (e) Gano, D. R.; Gordon, M. S.; Boatz, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6711.

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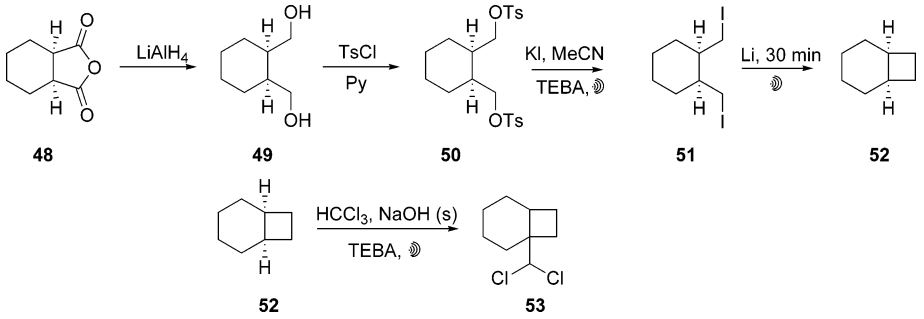

FIGURE 13. Synthesis of *cis*-bicyclo[4.2.0]octane and reaction with dichlorocarbene.

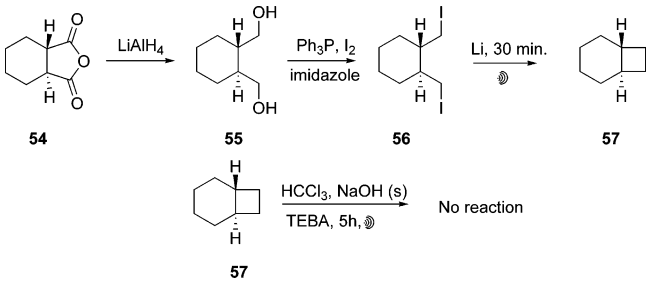

FIGURE 14. Synthesis of *trans*-bicyclo[4.2.0]octane and reaction with dichlorocarbene.

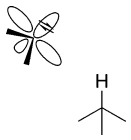

FIGURE 15. End-on mechanism.

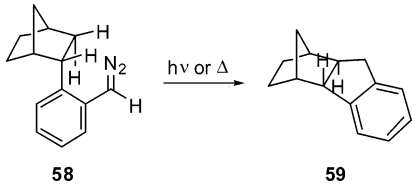

FIGURE 16. Example of a non-end-on mechanism.

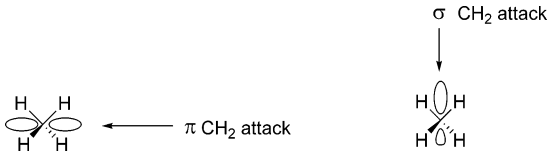

FIGURE 17. Different modes of insertion of mehtylene into methane.

propane was obtained.[64a] However, when the double bond is situated such that the C−H bond adjacent to the oxygen atom is also allylic (e.g. as in allyl ethyl ether), then this C−H linkage diverts some :CCl_2 from adding to the C−C double bond and an insertion product is also obtained.[5a,5c] This type of C−H bond is even more reactive with dihalocarbenes when it is contained in a five-membered ring.[4a,4b,5a,5c] Also, steric hindrance does appear to play a role. A *t*-butyl group strongly blocks dihalocarbenes from attacking at the geminal C−H bonds of Me_3CCH_2OMe.[64b] In a series of reactions with different ethers, dichlorocarbene gave insertion products with benzyl methyl

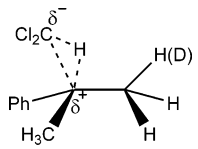

FIGURE 18. Transition state of dichlorocarbene insertion into a C−H bond.

ether (yield: 69%), isopropyl methyl ether (38%), and *n*-propyl methyl ether (10%).[5c] However, no insertion into the C−H bonds of the methyl group was observed in any case.

The insertion of dichlorocarbene is known to occur stereospecifically and with retention of configuration.[9e,65]

There are important factors which can affect the regio- and stereochemistry of insertion reactions. These are steric, electronic, and/or stereoelectronic effects. The known activating groups are not only heteroatoms such as oxygen, sulfur, or nitrogen, but also π orbital-containing groups such as phenyl, vinyl, and carbonyl.

All of these substituents can stabilize an adjacent partial cationic charge through their inductive (+I) or resonance (+R) effects. Based on the determination of primary[66] and β-secondary deuterium kinetic isotope effects[67] for the dichlorocarbene insertion into the *tertiary* C−H bond in cumene, a three-center transition state structure with partial charge separation, as depicted in Figure 18 was proposed.[67] Hyperconjugation stabilizes the partial positive charge developed on the carbon atom of the C−H bond to be inserted.[67]

The stabilization of a carbenium ion by an adjacent cyclopropane ring is a common phenomenon.[68] The Walsh orbitals of the three-membered ring can act as an electron donating group, much like the π orbitals of a double bond.[69,70]

A study of stabilization effects of the cyclopropyl group toward a carbenium ion showed that only when the cyclopropyl ring and the empty p orbital of the carbenium ion carbon can take on a certain conformation, namely the "bisected" one, the positive charge of the carbenium ion can be delocalized best (see Figure 19). In this rotamer, the Walsh orbitals of the three-membered ring and the p orbital of the carbenium ion are

(64) (a) Couch, E. V.; Landgrebe, J. A. *J. Org. Chem.* **1972**, *37*, 1251. (b) Seyferth, D.; Dertouzos, H. *J. Organometal. Chem.* **1968**, *11*, 263.

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(66) Seyferth, D.; Cheng, Y. M. *J. Am. Chem. Soc.* **1973**, *95*, 6763.
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(68) Carey, F. A., Ed. In *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984; Part A, pp 259−61.
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(70) (a) Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321. (b) Hanstein, W.; Berwin, H. J.; Taylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829.

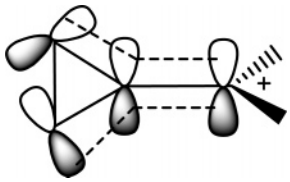


FIGURE 19. Overlap of the Walsh orbitals of the p orbital of the α carbon.

FIGURE 20. Orbital overlaps of Walsh orbitals and adjacent σ C−H orbitals.

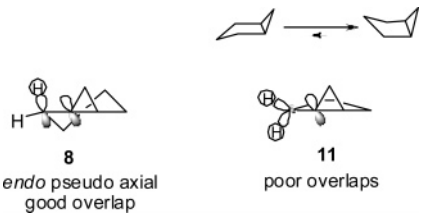


FIGURE 21. Orbital overlaps between Walsh orbitals and adjacent σ C−H bond orbitals.

aligned, thereby providing the maximum orbital overlap needed for stabilization (see Figure 20).

Calculations[63c] show that the insertion reaction of methylene into the C−H bonds of methane has an activation free energy close to zero or slightly negative. This suggests an early transition state. According to the Hammond postulate,[71] an early transition state implies that the activated complex resembles the reactant to a greater extent than the product. In this early transition state, the carbon bearing the C−H bond to be attacked has more sp^3 than sp^2 character, because there is no fully developed positive charge at any stage of the insertion reaction (see Figure 18).

Our recent work shows that dichlorocarbene inserts into norcarane **8**, producing as the major product, **9a**, which contained the dichloromethyl group *endo* to the three-membered ring.[1] In contrast, in the reaction of dichlorocarbene with bicyclo[3.1.0]hexane (**11**), the major insertion product **12b** has the dichloromethyl group located *exo* to the three-membered ring.[1] The magnitude of overlap between the Walsh orbitals and that of the α C−H σ-bond will affect the nucleophilicity of the C−H bond via delocalization of the electrons in the Walsh orbitals; the better the orbital alignment, the greater the effect. On one hand, little or no overlap between the Walsh orbitals and the adjacent α C−H bond σ-orbital will nullify any neighboring group participation leaving the α C−H bond in a nonactive state. On the other hand, partial to complete overlap of the orbitals may lead to a C−H bond that has been activated toward electrophilic carbene insertion (see Figure 21).

Inspection of molecular models of **8**[72] and **11**[72] reveals that the overlap of the orbitals of the *endo* C−H bonds at C2 and C5 of **8** with the Walsh orbitals of the three-membered ring is better than the corresponding interaction of the *endo* C−H bonds at C2 and C4 in **11**. In **8**, alignment of the σ orbitals of the *endo* C−H bonds at the α positions to the three-membered ring with the Walsh orbital seems to be better than with the corresponding *exo* C−H bonds. In bicyclo[3.1.0]hexane (**11**), the σ orbitals of the *exo* and *endo* C−H bonds at C2 and C4 seem to line-up with the Walsh orbitals to roughly the same extent. However, due to steric interactions with the flagpole hydrogen at C3 and the *endo* hydrogen at C6, preferential attack of dihalocarbenes should take place from the *exo* side. Therefore, **8** can serve as an example for the best overlap of orbitals, whereas there is less overlap in **11**.

In the reaction of spiro[2.5]octane (**46**) with dichlorocarbene almost no insertion products were formed, whereas 1-methyl-1-phenylcyclopropane (**47**) did not react at all. Study of a molecular model[72] of **46** shows that the four C−H bonds adjacent to the cyclopropane ring in spiro compound **46** do not take on geometries favorable for sufficient alignment with the Walsh orbitals. Consequently, dichlorocarbene insertion products are formed only in a very low yield (ca. 2%). Thus, the reactivity of **46** is comparable with that of cyclohexane under ultrasonication which affords a dichlorocarbene C−H bond insertion product only in trace amounts. Therefore, spiro[5.2]octane (**46**) serves as an example of the worst overlap of the Walsh orbitals with the σ orbitals of adjacent C−H bonds.

Dihalocarben(oid)s have been classified as electrophiles.[73] Thus, once they are generated either as "free" carbenes, or as carbenoids, they move toward the nucleophilic part of another available molecule where the electron density is highest. For compounds containing three-membered rings, the most nucleophilic area is where the Walsh orbitals of the three-membered ring are located (HOMOs). This situation is similar to the usual approach of electrophilic carbenes to double bonds, in which the empty p orbital of the carbene (LUMO) interacts with the filled orbital (HOMO) of the double bond.[3c] Dihalocarbenes, however, cannot formally add to a three-membered ring like they do to electron-rich double bonds. The C−H bonds of a three-membered ring, which have a similar degree of hybridization (such as sp^2 hybridized C−H bonds) are in general not inserted into by dihalocarbenes. As an allylic C−H bond is activated by the presence of an adjacent double bond,[74] for the reasons mentioned above, α C−H bonds should be more reactive toward electrophiles than any other C−H bonds in **8**.

Because of the difference in the magnitude of orbital overlap, the α *endo* C−H bonds in **8** are more nucleophilic than the corresponding *exo* C−H bonds. Furthermore, the overlap of the orbitals of the *endo* C−H bonds at C2 and C5 of **8** with the Walsh orbitals of the three-membered ring is better than the corresponding interaction of the *endo* C−H bonds at *C*2 and C4 in bicyclo[3.1.0]hexane (**11**). This difference in overlap probably accounts for the observed different stereoselectivity of the approaching dihalocarbenes.

At this point, it is instructive to compare the insertion reaction with other reactions that create or annihilate positive (partial) charges adjacent to cyclopropane rings. In fact, virtually no stereoselectivity is seen in solvolyses of the cyclopropylcarbinyl esters **60** and **61**. Although the bicyclo[4.1.0]heptane system[75]

(71) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

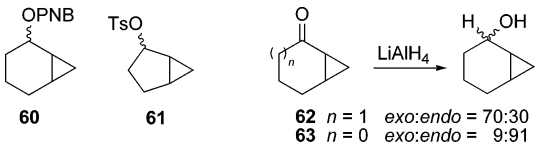
(72) 4−31G optimized geometries of **8** and **11** were taken from: Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85. See also: Kang, P.; Choo, J.; Jeong, M.; Kwon, Y. *J. Mol. Struct.* **2000**, *519*, 75.

(73) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, pp 274−7.

(74) March, J., Ed.; *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; Wiley: New York, 1992; pp 695−698.

(75) Gassman, P. G.; Creary, X. *J. Am. Chem. Soc.* **1973**, *95*, 6852.

is more reactive than the bicyclo[3.1.0]pentane system,[76] *exo* and *endo* isomers solvolyze at about the same rate in each case. The divergent observations can be explained by the "late" transition state of solvolysis reactions, where the stereoisomers give rise to the same cation. This is opposed to the "early" transition state of C−H insertion reactions which largely retains the configuration of the substrate.



On the other hand, the reduction of the bicyclo[n.1.0]-alkanones **62**[77] and **63**[78] shows stereoselectivity that is in accordance with that of dihalocarbene insertion. Here, a C−H bond is formed rather than broken, hence a "late" transition state accentuates the stereoselectivity.

The seven-membered ring in bicyclo[5.1.0]octane (**38**) is more flexible than the six-membered ring in bicyclo[4.1.0]heptane (**8**). According to molecular models, the orbital overlap of the Walsh orbitals of the three-membered ring and the orbitals of the adjacent C−H bonds seems to be less efficient than in **8** and **11**.

The separation of the products isolated from the reaction of bicyclo[5.1.0]octane (**38**) with dichlorocarbene showed that the two major products, **39a** and **39b**, were formed in a ratio of 2.4:1. Compared with the reaction of **8**, the yield of insertion products decreased from 83 to 65%. However, the stereochemical outcome of the reaction of **38** with dichlorocarbene is in line with that of the lower homolog, i.e., the norcarane **8**, where a 4:1 ratio of the *endo*−*exo* insertion products was observed. This further supports the concept that orbital overlap of the Walsh orbitals of the three-membered ring and the σ orbitals of the adjacent C−H bonds plays a key role in activating the α C−H bonds. Surprisingly, the ^{1}H NMR spectra of compounds **39a** and **39b** show nearly identical chemical shifts for the dichloromethyl groups at 5.92 and 5.91 ppm, respectively, while the coupling constants differ only slightly from each other. Unlike in the bicyclo[4.1.0]heptane series, in **9a** and **9b**, **18**, and **19**, one cannot determine the stereochemistry using the coupling constant of the proton at the dichloromethyl group and the adjacent proton on the seven-membered ring (vide infra).

The polarity of a solvent can affect the reaction path.[79] Depending on the polarity of the solvent, the reactions of dihalocarbenes with alkenes in different solvents often afford different product ratios.[80] Polar solvents stabilize polar intermediates. However, when the reaction of **8** was carried out in acetonitrile with dichlorocarbene generated by the ultrasonication method, no reaction took place. Perhaps the interaction of the dichlorocarbene with the nitrogen atom of acetonitrile is too strong, leading to rapid consumption of dichlorocarbene before it has a chance to interact with **8**. Similar results were observed when the reaction was carried out in pentane.

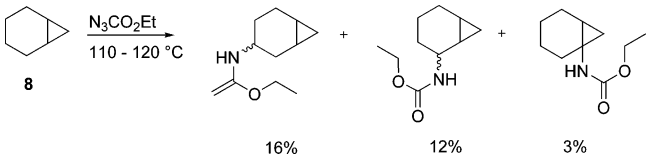


FIGURE 22. Reaction of norcarane with ethyl-α-azidoacetate.

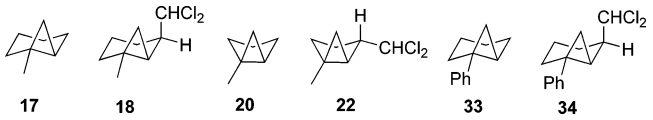


FIGURE 23. Substituted bicyclo[4.1.0]heptanes, bicyclo[3.1.0]hexanes and their dichlorocarbene insertion products.

The regiochemistry of the reaction of a nitrene[81] generated from the thermolysis of ethyl α-azidoacetate with bicyclo[4.1.0]-heptane (**8**) (Figure 22) is very different from what we report here with dihalocarbenes. No insertion products into β C−H bonds or the *tertiary* C−H bond of the three-membered ring were observed in our experiments.

In the reaction of **15a** and **15b** (ratio 7:1) with dichlorocarbene, in addition to insertion products **16a** and **16b**, five bis-insertion products were detected (see Figure 4). The double activation caused by the presence of two cyclopropane rings might be responsible for the formation of the bis-insertion products.

The introduction of substituents into bicyclo[4.1.0]heptane (**8**) is expected to change both the electron density distribution as well as the steric environment. Thus, when 1-methylbicyclo-[4.1.0]heptane (**17**) was reacted with dichlorocarbene, the insertion product, **18** (Figure 23), in which the *endo* C−H bond at C5 had been attacked by the carbene, was formed in a yield of 83%.

A similar result was obtained with 1-methylbicyclo[3.1.0]-hexane (**20**) and dichlorocarbene. Here, as expected, 4-*exo*-dichloromethyl-1-methylbicyclo[3.1.0]hexane (**22**) was isolated as the major insertion product. Obviously, the methyl group at C1 in **17** and **20** exerts an electronic and steric effect on the transition state of the reaction. In **17**, the steric effect of the methyl group guides the incoming dichlorocarbene more favorably toward the C5 position. The electronic effect of the methyl group seems to be smaller than its steric effect. If there were a strong electron donating effect, the electron density of the C−H bonds at C2 would be larger than at C5, and the insertion into the *endo* C−H bond at C2 would have been favored.

The reaction of 7,7-dimethylbicyclo[4.1.0]heptane (**23**) and dichlorocarbene afforded the two insertion products, **24a** and **24b** (*endo:exo* =1.13:1), in a yield of 55%. When compared with the reaction of bicyclo[4.1.0]heptane (**8**) and dichlorocarbene, the ratios of *endo*:*exo* insertion products have changed from 4:1 for **8** to 1.13:1 for **23**. The *endo*:*exo* ratios provide a hint about the nature of the transition states of the two reactions. Obviously, in **23** the steric effect of the methyl group in the *endo* position at C7 hinders the approaching dichlorocarbene from favorably interacting with the *endo*-hydrogens at C2 and C5. When compared with the parent system **8**, the presence of the 7-*endo* methyl group destabilizes the transition state and hence lowers the ratio of *endo* to *exo* isomers, as was observed.

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(80) Weber, J.; Brinker, U. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *37*, 1623.
(81) (a) Tardella, P. A.; Pellacani, L.; Di Statio, G. *Gazz. Chim. Ital.* **1972**, *102*, 822. (b) Tardella, P. A.; Pellacani, L. *Gazz. Chim. Ital.* **1973**, *103*, 337.

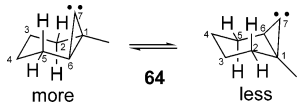

FIGURE 24. Two conformers of 1-methyl-7-norcaranylidene.

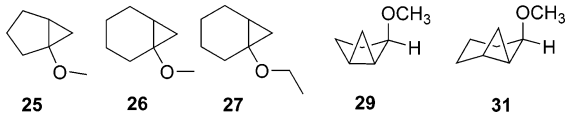

FIGURE 25. Bicyclo[4.1.0]heptanes and bicyclo[3.1.0]hexanes with an ether function at C1 and C2, respectively.

Therefore, dichlorocarbene attacks the C−H bonds at C2 and C5 in **23** from its *endo* and *exo* side to almost the same extent. The activation of the three-membered ring, however, is still strong enough to override the unfavorable steric effect introduced by the methyl groups at C7.

In contrast, when an electron-withdrawing substituent, such as a phenyl group, was introduced at C1 in **8**, the insertion reaction of **33** (Figure 23) with dichlorocarbene proceeded only sluggishly. In the same reaction time frame, the total yield of insertion products was only 30%, of which 64% resulted from insertions into the C−H bonds at C5. Apparently, the C2−H bonds are less reactive than the C5−H bonds. The −I effect of the phenyl group deactivates considerably the reactivity of the C−H bonds α to the three-membered ring. Because of the electron withdrawing effect of the phenyl group, the reaction of 1-phenylbicyclo[4.1.0]heptane (**33**) is favored at C5, as in the case of the 1-methyl-substituted compounds **17** and **20**. The +R effect of phenyl does not influence the reaction much, since it can only stabilize a benzylic position,[82] which in the case of **33** is occupied by the quaternary carbon C1. At the same time, the π orbitals of the phenyl substituent and the Walsh orbitals of the cyclopropane ring might interact, leading to an even larger delocalization of the electron density of the Walsh orbitals. By this means, the nucleophilicity of the cyclopropane ring to an approaching dihalocarbene would be reduced.

Studies of 1-methyl-substituted 7-norcaranylidenes **64** (Figure 24) showed that the methyl group somehow activates the C5−H bonds more than the C2−H bonds in intramolecular insertion reactions.[83]

It was speculated that in the preferred conformation of the transition state of 1-methyl-7-norcaranylidene, due to the presence of the methyl group at C1, the *endo* C5−H is in the axial position, and the *endo* C2−H bond is likely to be in an equatorial position.[83] Furthermore, in 1,2-hydrogen shifts, in general, preferentially the axial C−H is transferred to the divalent carbon.[84] The presence of a substituent at C1 can cause a molecule to take on a conformation in which the *endo* C5-H becomes axial while the *endo* C2−H is in an equatorial position. This also could explain the predominance of C5−H insertion products over C2−H ones in **17**, **20**, and **33**.

With ethers, dihalocarbenes can insert easily into the C−H bonds in α position to the oxygen atom. Obviously, the oxygen atom has a directional effect on the regiochemistry of the insertion reactions.

When 1-methoxybicyclo[4.1.0]heptane (**26**) (Figure 25) was reacted with dichlorocarbene, surprisingly no insertion reaction was observed at all. Not even a trace of any product resulting from insertion into the C−H bonds at C2 and/or C5 or any other C−H bonds could be detected. Instead, dichlorocarbene might have formed a complex[24,85] with the oxygen atom in **26**. As dichlorocarbene usually does not insert into the *primary* C−H bonds of a methyl group, **26** was totally recovered. A similar result was obtained with 1-methoxybicyclo[3.1.0]hexane (**25**).

In contrast, as anticipated, the reaction of 1-ethoxybicyclo[4.1.0]heptane (**27**) provided two products resulting from insertion into the C−H bonds α to the oxygen atom. It is interesting to note that in **25**, **26**, and **27** no insertion into the C−H bonds α to the three-membered ring took place. This shows that the activation or the nucleophilicity of the oxygen atom at C2 is stronger than that of the three-membered ring. From these observations, it is obvious that the deactivating effect of the alkoxy group at C1 in **25** and **26** overrides the activating effect exerted by the three-membered ring.

It was therefore no surprise that high yields of insertion products were obtained when 2-*endo*-methoxybicyclo[3.1.0]-hexane (**29**) and 2-*endo*-methoxybicyclo[4.1.0]heptane (**31**) were reacted with dichlorocarbene (95% and 94%, respectively). Though the C−H bonds at C2 in **29** and **31** are located at the *exo* position, insertion took place exclusively into these bonds. No insertion into the C−H bonds at C4 in **29** and C5 in **31**, respectively, was observed.

The reaction of *cis*-1,2-diethylcyclopropane (**41**) (Figure 11) with dichlorocarbene afforded **42a** and **42b** in a total yield of 30%. The ratio of the two products was 3:2. From the spectroscopic data, it was not possible to determine which of the two compounds was formed as the major isomer. When *trans*-1,2-diethylcyclopropane (**44**) was reacted with dichlorocarbene, two insertion products were obtained in a yield of 29% with a ratio of 1.3:1.

The reactions of *cis*-1,2-diethylcyclopropane (**41**) (Figure 11) and *trans*-1,2-diethylcyclopropane (**44**) with dichlorocarbene provide additional evidence that the interaction of the orbitals of the C−H bonds adjacent to the cyclopropane ring with the Walsh orbitals is the key factor responsible for the stereochemistry and the yield of the reaction. When compared with bicyclo[4.1.0]heptane (**8**), the free rotation of the two ethyl groups in both **41** and **44** makes orbital interaction less efficient. This leads to four similar C−H bonds adjacent to the three-membered ring which cannot be extensively differentiated by the approaching carbene. The three-membered rings in **41** and **44**, though, still have an activating effect on the C−H bonds in the α position.

The fact that *cis*-bicyclo[4.2.0]octane (**52**) (Figure 13) afforded a high yield of the insertion product which derives from insertion of $:CCl_2$ into the C−H bonds of the bridgehead

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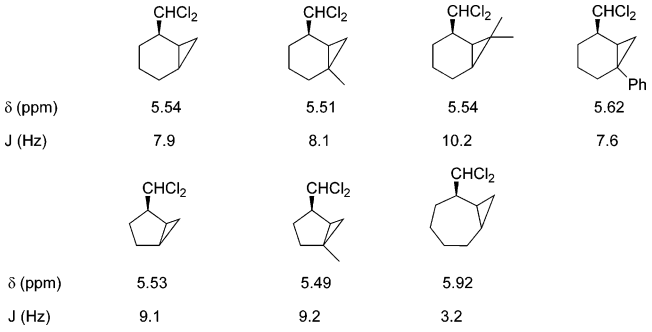

FIGURE 26. Chemical shifts and coupling constants of dichloromethyl groups in some bicyclo[n.1.0]alkanes.

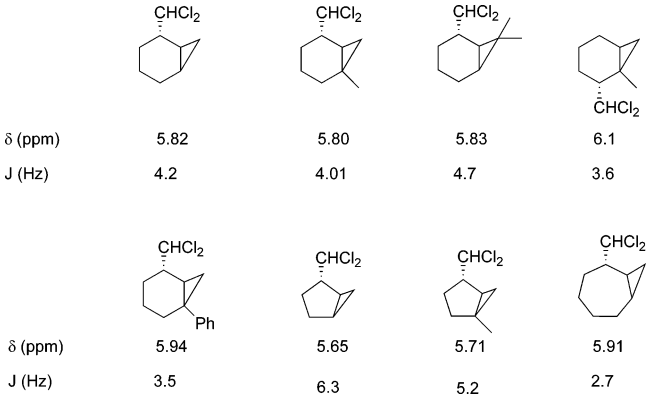

FIGURE 27. Chemical shifts and coupling constants of dichloromethyl groups in some bicyclo[n.1.0]alkanes.

carbons, suggests that the hyperconjugation of both *tertiary* C−H bonds might be an additional factor in the activation of these C−H bonds. The main factor, however, seems to be the spatial availability of the *tertiary* C−H bonds. In *trans*-decalin **7** and *trans*-bicyclo[4.2.0]octane (**57**) there are no such alignments. In addition, the *tertiary* C−H bonds are well hidden within the molecule frame. Insertion reactions into those C−H bonds, therefore, fail, or take place only to a minor extent. This suggests that the interactions between the Walsh orbitals of cyclopropane rings and the orbitals of suitably positioned adjacent C−H bonds are quite different from those of cyclobutane rings. While some cyclopropane rings activate *adjacent* C−H bonds, the cyclobutane ring in **52** obviously does not. In insertion reactions, the four-membered ring, therefore, behaves like the five-membered ring in dodecahedrane (**3**)[22] and the six-membered rings in adamantane,[20,21] where only insertion into the *tertiary* C−H bonds has been reported.

Chemical Shifts and Coupling Constants of Some Bicyclo[n.1.0]alkanes. Throughout this work, the stereochemistry of the $CHCl_2$ group was ascertained by 1D NOE difference spectroscopy. From Figure 26, it is seen that compounds containing an *endo* dichloromethyl group have a coupling constant of ca. 8−10 Hz and that the magnitude of the vicinal coupling constants of the proton of the dichloromethyl group with the proton on the ring correlates well with the stereochemical relationship of the dichloromethyl group and the three-membered ring.

In contrast, in the bicyclo[4.1.0]heptane and bicyclo[3.1.0]-hexane series (Figure 27), the *exo* isomers have smaller coupling constants, ca. 3−6 Hz. However, this does not apply to the bicyclo[5.1.0]octane system, where the corresponding vicinal coupling constants are virtually identical.

Conclusion

Dihalocarbenes are highly electron deficient and electrophilic. Although they approach the C−H bond, a partial cationic character develops on the carbon of the C−H bond to be inserted. The stability of this species is the key factor governing the formation of the products. The more stabilized this species is, the faster it should be formed.

Electron-donating groups or heteroatoms can stabilize the developing partial positive charge through an inductive or resonance effect. The electrophilic dihalocarbenes interact first with the more nucleophilic part of the molecule. In compounds containing three-membered rings that part is the cyclopropane ring with its Walsh orbitals.

The activation of the C−H bonds is determined by the efficiency of the initial interaction of the orbitals between the σ and the Walsh orbitals. In bicyclo[4.1.0]heptane (**8**), the *endo* C−H bonds interact better with the Walsh orbitals of the cyclopropane ring than the corresponding *exo* C−H bonds do. The overlap of the Walsh orbitals with the adjacent *endo* C−H bonds is better in bicyclo[4.1.0]heptane (**8**) than in bicyclo-[3.1.0]hexane (**11**). The seven-membered ring in bicyclo[5.1.0]-octane (**38**) is more flexible than the corresponding rings in bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane. Therefore, the magnitude of overlap of the *endo* C−H bonds with the Walsh orbitals is less efficient in **38** than in bicyclo[4.1.0]heptane (**8**). In addition, in *cis*- and *trans*-diethylcyclopropane, **41** and **44**, the four C−H bonds in α position to the three-membered ring seem to interact less efficiently with the Walsh orbitals. This fact could explain the lower yield of insertion products.

Dihalocarbenes can insert into a C−H bond when three factors are present: (1) the C−H bond is spatially available, i.e., it is not barred by other bonds; (2) the C−H bond is located in a position close to group(s) and/or atoms which can stabilize a developing positive charge through resonance dispersion and/or inductive effects (as in the C−H bonds adjacent to three-membered rings); and (3) the orientation of the C−H bond favors interaction with the Walsh orbitals of an adjacent cyclopropane ring.

Experimental Section

Starting Materials. Bicyclo[4.1.0]heptane (**8**), bicyclo[3.1.0]-hexane (**11**), tricyclo[5.1.0]octane (**38**), spiro[2.5]octane (**46**), and 1-methyl-1-phenylcyclopropane (**47**) were prepared from cyclohexene, cyclopentene, cycloheptene, methylenecyclohexane, and α-methylstyrene, respectively.

General Procedure for Ultrasonicated Dihalocarbene Insertions into α C−H Bonds of Cyclopropanes and the Bridgehead C−H Bond of *cis*-Bicyclo[4.1.0]octane. *Dichlorocarbene Insertions.* A mixture of 0.01 mol of hydrocarbon and 10 g of fine powdered sodium hydroxide was added to a 50 mL round-bottomed flask fitted with a reflux condenser and a drying tube. The flask was immersed in the water bath of an ultrasonic cleaner and placed about 0.5 cm above the horn. After addition of 25 mL of chloroform and 0.03 g of triethylbenzylammonium chloride (TEBA) through the top of the reflux condenser, the reaction mixture was ultrasonicated for 3 h. (The water in the bath and the reaction mixture in the flask should be kept at the same level. It is not necessary to control the temperature of the water bath during ultrasonication.) After removal of inorganic substances by filtration (using Celite

535 as filtration aid), the filtrate was concentrated using a Rotavapor. 20 mL of pentane and 5 g of silica gel were added to the residue, and the mixture was filtered again. The pentane was removed by a Rotavapor and the obtained yellowish oil was further purified by preparative GC or HPLC.

Dibromocarbene Insertions. A mixture of 5.1 g (0.02 mol) of bromoform, 25 mL of dichloromethane and 0.1 g of TEBA was used. Otherwise, the experimental conditions are the same as those described for the *dichlorocarbene insertion* procedure.

***endo*-2-Dichloromethylbicyclo[4.1.0]heptane (9a)**. (PGC separation on column G). ^{1}H NMR (360 MHz) d 5.54 (d, 1H, J = 7.9 Hz), 2.43−2.53 (m, 1H), 1.94−2.04 (m, 1H), 1.78−1.87 (m, 1H), 1.46−1.56 (m, 1H), 1.25−1.36 (m, 1H), 1.11−1.24 (m, 2H), 1.01−1.11 (m, 1H), 0.73−0.85 (m, 1H), 0.64 (dt, 1H, J = −4.9 Hz, 8.8 Hz), 0.12 (dt, 1H, J = −4,9 Hz, 5.3 Hz). ^{13}C NMR (90.6 MHz) δ 78.8 (d, J = 174 Hz), 45.3 (d, J = 126 Hz), 23.4 (t, J = 130 Hz), 23.3 (t, J = 130 Hz), 22.4 (t, J = 127 Hz), 13.2 (d, J = 161 Hz), 9.9 (d, J = 160 Hz), 8.5 (t, J = 160 Hz). IR (film) ν 3080, 3015, 2940, 2862, 1463, 1312, 1230, 1212, 1105, 1080, 1025, 1000, 888, 860, 830, 780, 747, 730, 680, 640 cm^{-1}. MS (70 eV) *m*/*e* (%) 178, 180, 182 (M^+, 0.45, 0.28, 0.04), 143, 145 (7, 2), 142, 144 (2, 1), 129, 131 (17, 5), 115, 117 (3, 1), 107 (12), 102, 104 (6, 2), 96 (10), 95 (100), 93 (13), 91 (11), 88 (25), 79 (20), 77 (18), 67 (50), 65 (14), 55 (16), 53 (16), 41 (22), 39 (26). Anal. Calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75. Found: C, 53.59; H, 6.78.

***exo*-2-Dichloromethylbicyclo[4.1.0]heptane (9b)**. (PGC separation on column E, purity, 67%, containing 33% of **9a**). ^{1}H NMR (360 MHz) δ 5.82 (d, 1H, J = 4.2 Hz), 2.17−2.27 (m, 1H), 1.76−1.92 (m, 1H), 1.62−1.76 (m, 1H), 1.45−1.55 (m, 2H), 0.91−1.25 (m, 3H), 0.66 (dt, 1H, J = −4.9 Hz, 5.3 Hz), 0.12 (dt, J = −4.9, 8.8 Hz). ^{13}C NMR (90.6 MHz) δ 78.7 (d), 43.0 (d), 25.5 (t), 22.7 (t), 21.3 (t), 18.2 (t), 12.1 (d), 10.6 (d). MS (70 eV) *m*/*e* (%) 178, 180, 182 ($M^{+\cdot}$, 0.95, 0.64, 0.08), 143, 145 (7, 2), 142, 144 (2, 1), 129, 131 (17, 5), 115, 117 (4, 2), 107 (23), 102, 104 (4, 1), 101, 103 (9, 4), 96 (8), 95 (100), 93 (18), 91 (14), 88 (33), 79 (26), 77 (17), 67 (45), 65 (14), 55 (14), 53 (13), 41 (12), 39 (14).

***endo*-2-Dibromomethylbicyclo[4.1.0]heptane (10a)**. (HPLC and then PGC separation on column D at T_c = 120 °C; T_i = 150 °C; and T_d = 130 °C). ^{1}H NMR (360 MHz) δ 5.52 (d, 1H, J = 7.8 Hz), 2.43−2.61 (m, 1H), 1.77−2.02 (m, 2H), 1.45−1.56 (m, 1H), 1.14−1.40 (m, 3H), 1.00−1.12 (m, 1H), 0.68−0.82 (m, 1H), 0.64 (dt, 1H, J = −5.0, 8.9 Hz), 0.14 (dt, 1H, J = −5.0, 5.4 Hz). ^{13}C NMR (90.6 MHz) δ 54.1 (d, J = 176 Hz), 45.9 (d, J = 130 Hz, *C*2), 25.1 (t, J = 129 Hz, C3), 23.4 (t, J = 126 Hz), 22.9 (t, J = 127 Hz), 14.7 (d, J = 167 Hz), 10.3 (d, J= 162 Hz), 8.6 (t, J = 159 Hz). IR (film) ν 3080, 3020, 2945, 2870, 1468, 1458, 1312, 1240, 1153, 1110, 1080, 1028, 1000, 888, 860, 835, 770, 740, 675, 635, 618 cm^{-1}. MS (70 eV) *m*/*e* (%) 187, 189 ([M−Br]$^+$, 19.6, 19.6), 171, 173, 175 (2, 4, 3), 160, 162 (2.5, 2.5), 159, 161 (2, 2), 146, 148 (2, 2), 145, 147 (4, 5), 132, 134 (15, 15), 119, 121 (10, 8), 107 (78), 95 (100), 93 (15), 91 (25), 81 (22), 79 (80), 77 (22), 67 (58), 65 (22), 55 (23), 53 (30), 41 (32), 39 (37).

***exo*-2-Dibromomethylbicyclo[4.1.0]heptane (10b)**. (Obtained from a mixture with **10a** after HPLC separation. **10b** decomposes under PGC conditions). ^{1}H NMR (360 MHz) δ 5.83 (d, 1H, J = 3.7 Hz), 2.69−2.79 (m, 1H), 0.70 (dd, 1H), 0.49 (dt, J = −4.3 Hz, 8.8 Hz), 0.04 (dt, J = −4.3, 4.5 Hz, *endo* H-C7), other signals overlap with signals of **10a**. ^{13}C NMR (90.6 MHz) δ 54.7 (d, J = 175 Hz), 47.6 (d, J = 133 Hz), 27.4 (t), 22.7 (t), 18.2 (t), 14.1 (d, J = 164 Hz), 10.9 (d, J = 161 Hz), 9.0 (t, J = 163 Hz). MS (70 eV) *m*/*e* (%) 187, 189 ([M−Br]$^+$, 20, 24), 173, 175 (3, 4), 160, 162 (3, 2), 159, 161 (3, 3), 146, 148 (2, 3), 145, 147 (6, 6), 132, 134 (20, 19), 119, 121 (11, 10), 107 (100), 95 (55), 93 (16), 91 (33), 81 (21), 79 (91), 77 (25), 67 (52), 65 (26), 55 (24), 53 (30), 41 (34), 40 (69), 39 (42).

***exo*-Dichloromethylbicyclo[3.1.0]hexane (12b)**. (PGC separation on Column E or F). ^{1}H NMR (360 MHz) δ 5.65 (d, 1H, J = 6.3 Hz), 2.64 (dd, 1H), 1.75−1.97 (m, 2H), 1.63−1.72 (m, 2H), 1.35−1.50 (m, 2H), 0.53 (dt, J = −5.1, 8.2 Hz), 0.14 (dt, J = −5.1, 3.9 Hz). ^{13}C NMR (90.6 MHz), δ 77.6 (d, J = 177 Hz), 52.7 (d), 26.1 (t), 24.6 (t), 19.9 (d, J = 170 Hz), 17.3 (d, J = 166 Hz), 7.3 (t, J = 157 Hz). IR (film) ν 3080, 3045, 3005, 2945, 2875, 1468, 1450, 1270, 1255, 1218, 1922, 940, 908, 855, 813, 790, 758, *735*, 700, 660, 645 cm^{-1}. MS (70 eV) *m*/*e* (%) 164, 166 ($M^{+\cdot}$, 0.3, 0.2), 129, 131 (6, 2), 115, 117 (3, 1), 101, 103 (1.3, 0.5), 93 (19), 91 (8), 88 (7), 81 (100), 79 (27), 77 (11), 67 (5), 65 (7), 54 (7), 53 (14), 51 (6), 41 (11), 39 (14). Anal. Calcd for $C_7H_{10}Cl_2$: C, 50.94; H, 6.11. Found: C, 50.66; H, 6.05.

***endo*-Dichloromethylbicyclo[3.1.0lhexane (12a)**. (PGC separation on Column E or F). ^{1}H NMR (360 MHz) δ 5.53 (d, 1H, J = 9.1 Hz), 2.83−2.93 (m, 1H), 0.36 (m, 2H), others signals overlap with the signals of **12b**. ^{13}C NMR (90.6 MHz) δ 78.0 (d), 53.0 (d), 25.8 (t), 25.2 (t), 19.6 (d), 18.9 (d), 3.9 (t).

***exo*-Dibromomethylbicyclo[3.1.0]hexane (13b)**. (HPLC separation). ^{1}H NMR (360 MHz) δ 5.64 (d, 1H, J = 6.0 Hz), 2.78 (dd, 1H, H-*C*2), 1.50−1.61 (m, 2H), 1.30−1.50 (m, 2H), 1.12−1.25 (m, 2H), 0.55 (dt, J = −4.8, 8.2 Hz), 0.14 (dt, J = −4.8, 4.2 Hz). ^{13}C NMR (90.6 MHz) δ 53.6 (d), 40.8 (d), 27.0 (t), 20.7 (t), 20.2 (d), 17.6 (d), 7.7 (t). MS (70 eV) *m*/*e* (%) 252, 254, 256 ($M^{+\cdot}$, 1, 2, 1), 210, 212, 214 (17, 35, 17), 197, 199, 201 (2.4, 5, 2.6), 173, 175 (11, 10), 131, 133 (7, 8), 93 (52), 91 (17), 79, 81 (11, 10), 77 (21), 68 (100), 67 (34), 65 (15), 55 (21), 51 (10), 41 (10), 39 (20).

***endo*-Dibromomethylbicyclo[3.1.0]hexane (13a).** (HPLC separation). ^{1}H NMR (360 MHz) δ 5.50 (d, 1H, J = 9.6 Hz), 2.95−3.09 (m, 1H), 0.30−0.42 (m, 2H) other signals overlap with signals of **13b**. ^{13}C NMR (90.6 MHz) δ 54.0 (d), 46.0 (d), 26.5 (t), 26.2 (t), 22.0 (d), 21.7 (d), 3.6 (t). MS (70 eV) *m*/*e* (%) 252, 254, 256 ($M^{+\cdot}$, 0.1, 0.2, 0.1), 173, 175 (14, 13), 132, 134 (4, 4), 119, 121 (7, 7), 93 (82), 91 (22), 81 (100), 79, 81 (27, 100), 77 (30), 67 (10), 65 (12),54 (12), 53 (17), 51 (8), 41 (14), 40 (12), 39 (24).

2-Dichloromethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane (16a). (PGC separation on column E). ^{1}H NMR (360 MHz) δ 5.82 (d, 1H, J = 6.0 Hz), 2.24 (ddd, 1H, J = −14.7, 8.4, 2.7 Hz), 2.15−2.21 (m, 1H), 1.29 (ddd, 1H, J = −14.7 Hz, 6.0 Hz, 2.9 Hz), 1.02 (m, 1H), 0.85−0.96 (m, 2H), 0.49−0.67 (m), 0.43 (dt, J = −5.0, 8.1 Hz), −0.18 (dt, J = −5.0, 5.0 Hz). ^{13}C NMR (90.6 MHz) δ 79.0 (d, J = l77 Hz), 46.5 (d, J = 135 Hz), 22.3 (t, J = 127 Hz), 15.1 (t, J = 159 Hz), 10.4 (d, J = 153 Hz), 8.8 (d, J = 160 Hz), 8.6 (d, J = 163 Hz), 4.7 (d, J = 160 Hz), 3.9 (t, J = 155 Hz). IR (film) ν 3075, 3010, 2925, 2858, 1471, 1450, 1270, 1211, 1150, 1125, 1095, 1027, 985, 973, 913, 865, 840, 828, 812, 790, 740, 670 cm^{-1}. MS (70 eV) *m*/*e* (%) 155, 157 ([M−Cl]$^+$, 7.0, 2.2), 141, 143 (5.9, 2.0), 136, 138 (4.3, 2.7), 128, 130 (4.0, 1.3), 127, 129 (3.3, 1.1), 119 (13), 115 (6), 113 (8), 107 (14), 105 (13), 101, 103 (52, 21), 91 (45), 88 (26), 79 (100), 77 (33), 67 (34), 65 (25), 54 (13), 53 (10), 51 (11), 41 (15), 39 (18). Anal. Calcd for $C_9H_{12}Cl_2$: C, 56.57; H, 6.33. Found: C, 56.30; H, 6.28.

2-(*endo*)-Dichloromethyl-*syn*-tricyclo[5.1.0.0^{3,5}]octane (16b). (PGC separation on column E). ^{1}H NMR (360 MHz) δ 5.45 (d, 1H, J = 9.6 Hz), 3.04 (dt, 1H, J = 9.6, 5.9 Hz), 2.20 (dt, 1H, J = −14.4, 6.8 Hz), 2.03 (d, 1H, J = −14.4, 0.8 Hz), 1.13−1.24 (m, 2H), 1.02−1.12 (m, 2H), 0.38 (dt, 2H, J = −5.5, 9.2 Hz), −0.18 (dt, 2H, J = −5.4, 5.6 Hz). ^{13}C NMR (90.6 MHz) δ 78.9 (d, J = 178 Hz), 40.7 (d, J = 132 Hz), 17.9 (t, J = 127 Hz), 11.5 (d, J = 164 Hz), 10.9 (d, J = 161 Hz), 8.1 (t, J = 166 Hz). MS (70 eV) *m*/*e* (%). *endo* isomer: 155, l57 ([M−Cl]$^+$, 6.5, 2.0), 149, 151 (4, 3), 136, 138 (3, 2), 128, 130 (4, 1), 127, 129 (4, 1), 119 (16), 115 (9), 113 (15), 107 (17), 105 (7), 101, 103 (27, 14), 91 (48), 88 (15), 79 (75), 77 (38), 67 (100), 65 (33), 54 (27), 53 (15), 51 (19), 41 (30), 40 (47), 39 (37). *exo* isomer: 155, 157 ([M−Cl]$^+$, 0.7, 0.3), 127, 129 (1, 0.4), 119 (2), 115 (2), 113 (3), 107 (42), 105 (6), 101, 103 (6, 4), 91 (25), 88 (4), 79 (100), 77 (21), 67 ([C_5H_7]$^+$, 15), 65 (14), 54 (6), 53 (7), 51 (8), 41 (15), 40 (13), 39 (16). It is assumed that the *endo* isomer has a shorter GC retention time than the *exo* isomer.

2,6-Bis(dichloromethyl)tricyclo[5.1.0.0^{3,5}]octane (5 isomers)*. (HPLC separation). ^{1}H NMR (360 MHz) δ Isomer-1 (1.6%): 6.02 (d, J = 5.5 Hz); Isomer-2 (10.5%): 5.87 (d, J = 5.6 Hz), 2.14−

2.19; Isomer-3 (29.7%): 5.45 (d, $J = 9.3$ Hz), 3.00−3.19; Isomer-4 (36.3%): 5.99 (d, $J = 2.3$ Hz), 5.56 (d, $J = 9.2$ Hz), 3.11 (dt, $J = 9.3, 6.2$ Hz), 2.85 (bd, $J = 2.3$ Hz); Isomer-5 (21.9%): 5.67 (d, $J = 6.9$ Hz), 2.61−2.67. Isomer-3 is suggested to be 2-(*endo*),6-(*endo*)-bisdichloromethyl-*syn*-tricyclo[5.1.0.0^{3,5}]octane based on the coupling constants. Isomer-4 is thought to be 2-(*endo*),6-(*exo*)-bisdichloromethyl-*syn*-tricyclo[5.1.0.0^{3,5}]octane. ^{13}C NMR (90.6 MHz) δ for CCl_2: 79.3, 78.2, 78.0, 77.9, 77.8 (d, $J = 177$ Hz); δ for *C*2/3: 46.7 (d, $J = 133$ Hz), 43.1 (d, $J = 134$ Hz), 40.9 (d, $J = 130$ Hz), 40.2 (d, $J = 132$ Hz), 39.8 (d, $J = 135$ Hz). Only four isomers can be observed. IR (film) ν 3080, 2990, 2925, 2900, 1472, 1445, 1380, 1320,1280, 1200, 1025, 970, 936, 890, 850, 830, 813, 740, 685, 665, 635 cm^{-1}. MS (70 eV) *m*/*e* (%) Isomer-1 (0.9% on GC, $t_R = 9.44$ min) 237 ([M-C1]$^+$, 4), 201, 203 (7, 6), 189 (4), 173, 175 (3, 2), 165, 167 (8, 3), 161, 163, 165 (4, 3, 8), 153, 155 (11, 3), 149, 151 (18, 14), 136, 138, 140 (17, 12, 4), 129 (15), 127 (14), 125 (16), 117 (21), 115 (27), 113 (47), 103 (29), 101 (80), 91 (41), 88 (28), 79 (30), 77 (59), 75 (32), 65 (42), 51 (30), 40 (100), 39 (36). Isomer-2 (14.4% on GC, $t_R = 9.86$ min) 237, 239 ([M-C1]$^+$, 0.5, 0.5), 223, 225 (0.4, 0.4), 201, 203 (1.5, 0.6), 189, 191, 193 (4, 2, 0.3), 165, 167 (2, 1), 161, 163, 165 (2, 1.4, 2), 153, 155 (11, 4), 149, l51 (3, 2), 136, 138, 140 (32, 21, 4), 129 (6), 127 (10), 125 (14), 117 (26), 115 (14), 113 (11), 103 (36), 101 (100), 91 (32), 88 (15), 79 (19), 77 (32), 75 (18), 65 (24), 51 (16), 41 (13), 39 (19). Isomer-3 (25.8% on GC, $t_R = 10.01$ min) 237, 239 ([M-C1]$^+$, 0.4, 0.3), 223, 225, 227 (0.4, 0.4, 0.1), 201, 203 (1, 0.8), 189, 191, 193 (2.6, 1.3, 0.3), 165, 167 (2, 1), 161, 163, 165 (3, 2, 2), 153, 155 (10, 3), 149, 151 (3, 2), 136, 138, 140 (23, 15, 3), 129 (5), 127 (10), 125 (14), 117 (26), 115 (13), 113 (10), 103 (36), 101 (100), 91 (30), 88 (14), 79 (16), 77 (28), 75 (17), 65 (21), 51 (12), 41 (8), 39 (14). Isomer-4 (34.8% on GC, $t_R = 10.28$ min) 237, 239 ([M−Cl]$^+$, 0.4, 0.4), 223 (0.2), 201, 203, 205 (1.8, 1.2, 0.3), 189, 191, 193 (33, 22, 3), 165, 167 (4, 1), 161, 163, 165 (6, 4, 4), 153, 155 (43, 14), 149, 151 (5, 3), 136, 138, 140 (8, 6, 2), 129 (12), 127 (27), 125 (45), 117 (100), 115 (33), 113 (28), 103 (27), 101 (55), 91 (83), 88 (15), 87 (16), 79 (44), 77 (63), 75 (41), 65 (37), 51 (27), 41 (20), 39 (27). Isomer-5 (24.1% on GC, $t_R = 10.54$ min) 237, 239 ([M-C1]$^+$, 0.4, 0.2), 223, 225 (0.2, 0.3), 201, 203 (0.9, 0.6), 189, 191, 193 (26, 16, 3), 165, 167 (3, 1), 161, 163, 165 (6, 4, 3), 153, 155 (52, 16), 149, 151 (3, 3), 136, 138, 140 (14, 10, 3), 129 (11), 127 (33), 125 (42), 117 (100), 115 (33), 113 (24), 103 (27), 101 (58), 91 (94), 89 (12), 88 (12), 87 (13), 85 (11), 83 (16), 79 (50), 77 (58), 75 (43), 65 (35), 51 (25), 41 (19), 39 (27).* The sequence numbers of the isomers are according to their retention times (GC conditions: $T_i = 250$ °C; $T_c = 120$ °C (1 min) → 20 °C/min → 240 °C; $T_d = 280$ °C).

Dichloromethylspiro[2.5]octane (3 isomers in a ratio of 4.8:1:1.2). (PGC Separation on column G). ^{1}H NMR (360 MHz) δ 6.08 (d, $J = 9.6$ Hz, rel. content: 69%), 5.72 (d, $J = 4.2$ Hz, rel. content: 14%), 5.67 (d, $J = 4.7$ Hz, rel. content: 17%), 0.15−0.52 (m), 0.65−2.18 (m). ^{13}C NMR (90.6 MHz) δ the major isomer 76.1 (d), 52.9 (d), 31.5 (t), 28.0 (t), 24.9 (t), 20.6 (t), 14.5 (t), 11.6 (t), one quaternary carbon signal is missing. MS (70 eV) *m*/*e* (%) Isomer-1 (16.8% on GC, $t_R = 8.97$ min) 192, 194, 196 (M$^{+\cdot}$, 5.4, 3.5, 0.53), 164, 166 (2, 1), 157, 159 (5, 2), 143, 145 (1.3, 0.4), 129, 131 (10, 2)$^+$, 127, 129 (11, 10), 122 (11), 121 (20), 109 (100), 107 (13), 93 (16), 91 (23), 88 (12), 81 (37), 79 (36), 77 (17), 67 (69), 65 (11), 55 (17), 53 (19), 51 (11), 41 (27), 39 (29); Isomer-2 and −3 (83.2 on GC, $t_R = 9.06$ min) 192, 194, 196 (M$^{+\cdot}$, 1.2, 0.7, 0.1), 164, 166, 168 (0.8, 0.4, 0.1), 163, 165, 167 (0.9, 0.7, 0.2), 157, 159 (5, 2), 143, 145 (1.7, 0.4), 130, 132 (5, 2), 129, 131 (10, 4)$^+$, 121 (14), 109 (100), 93 (12), 91 (10), 88 (5), 81 (36), 79 (20), 77 (12), 67 (42), 65 (7), 55 (9), 54 (6), 53 (7), 51 (6), 41 (9), 39 (9). (GC conditions: $T_i = 250$ °C; $T_c = 70$ °C (1 min) → 20 °C/min → 210 °C; $T_d = 280$ °C).

Dichloromethylcyclohexane.[86] (PGC separation on column E). ^{1}H NMR (360 MHz) δ 5.66 (d, $J = 3.9$ Hz, $HCCl_2$), 1.87−1.99 (m, 3H), 1.78−1.87 (m, 2H), 1.65−1.73 (m, 2H), 1.18−1.31 (m, 4H). ^{13}C NMR (90.6 MHz) δ 78.8 (d, $J = 177$ Hz), 48.4 (d, $J = 125$ Hz), 28.3 (t, $J = 128$ Hz), 25.9 (t, $J = 128$ Hz), 25.5 (t, $J = 127$ Hz). IR (film) ν 2985, 2935, 2860, 1740, 1555, 1450, 1390, 1365, 1296, 1250, 1215, 1160, 1130, 1102, 1060, 1020, 960, 920, 877, 852, 788, 740, 713, 677, 643, 601 cm^{-1}. MS (70 eV) *m*/*e* (%) 166, 168 (M$^+$, 0.6, 0.4), 84 (7), 83 (100), 82 (13), 55 (33), 41 (11), 39 (7).

General Procedure for the Cyclopropanation of Alkenes in the Presence of the CH_2Br_2/Zn/CuCl System Using Ultrasound.[33b] A 250 mL three-necked flask equipped with reflux condenser, dropping funnel, and mechanical stirrer was charged with 39 mmol of zinc dust, which was activated as follows: To a hot, rapidly stirred solution of 2.0 g of cupric acetate monohydrate in 50 mL of glacial acetic acid was added 35 g of zinc dust. After about 0.5−1 min, all of the copper had deposited on the zinc. The couple was allowed to settle for 0.5−1 min. The dark reddish-gray couple was then washed with one 50 mL portion of acetic acid, followed by three 100 mL portions of ether. The moist zinc/copper couple was ready for use. Four mmol of CuCl powder and 20 mmol of CH_2Br_2 in 25 mL of dry ether (distilled over Na) were added to the flask. The reaction mixture was ultrasonicated together with a mechanical stirrer for 30 min. In general, the reaction mixture turned to dark red-gray. 10 mmol of alkene in 20 mL of ether were added dropwise within 30 min, and depending on the completion of the reaction, the reaction mixture was ultrasonicated for an additional 2−3 h. Gas chromatography was used to monitor the reaction progress until the starting material had disappeared (2−4 h). The reaction mixture was diluted with 100 mL of dry ether, and filtered through a layer of Celite. The Celite was rinsed with 100 mL of ether and the combined filtrate was washed with saturated NH_4Cl solution and brine, and dried over $MgSO_4$. After removal of the drying reagent, the ether was evaporated and the resulting residue distilled (760 mmHg). Yield of the products: 50−85%.

***syn*-Tricyclo[5.1.0.0^{3,5}]octane (15b)**.[44] (PGC separation on column E). ^{1}H NMR (360 MHz) δ 2.37−2.49 (m, 2H), 0.79−0.91 (m, 4H), 0.67−0.76 (m, 2H), 0.64 (dt, 2H, $J = 4.6, 8.3$ Hz), −0.19 [dt, 2H, $J = -4.6, 4.6$ Hz). ^{13}C NMR (90.6 MHz) δ 24.6 (t, $J = 126$ Hz), 15.5 (t, $J = 158$ Hz,), 9.9 (d, $J = 162$ Hz).

1-Methylbicyclo[4.1.0]heptane (17).[87] **17** was synthesized from 9.6 g (10 mmol) 1-methylcyclohexene according to the general procedure. 7.7 g was obtained. Yield: 70%. ^{13}C NMR (90.6 MHz) δ 15.3 (q), 30.8 (t), 21.6 (t), 21.9 (t), 24.3 (t), 18.4 (d), 17.9 (t), 27.9 (q).

5-*endo*-Dichloromethyl-1-methylbicyclo[4.1.0]heptane (18). 0.55 g (5 mmol) of **17** was ultrasonicated for 3 h according to the general procedure. 0.83 g was obtained. Column D was used to separate the isomers. Yield: 87%. ^{1}H NMR (360 MHz) δ 5.49 (1H, d, $J = 8.1$ Hz), 2.53−2.45 (1H, m), 1.85−1.73 (2H, m), 1.69−1.63 (2H, m), 1.51−1.41 (2H, m), 1.09 (3H, s), 0.99 (1H, dt, $J = 5.3, 8.8$ Hz), 0.37 (1H, dd, $J = 4.7, 8.9$ Hz), 0.29 (1H, t, $J = 5.2$ Hz). ^{13}C NMR (90.6 MHz) δ 78.7, 45.2, 27.6, 23.3, 21.8, 21.7, 18.5, 15.3. IR (film) ν 3060, 2994, 2936, 2861, 1452, 1380, 1312, 1213, 1029, 953, 775, 745, 684 cm^{-1}. MS (70 eV) *m*/*e* (%) 194, 192 (M$^+$, 1.1, 1.7), 157 (4.1), 156 (2.6), 145, 143 (5.8, 17.9), 129, 127 (2.9, 2.3), 122 (2.6), 121 (14.5), 115 (5.3), 110 (8.7), 109 (100), 107 (7.9), 105 (6.5), 101 (3.9), 95 (6.7), 94 (3.4), 93 (14.1), 92 (2.6), 91 (15.6), 90 (11.3), 89 (5.9), 88 (32.9), 85 (3.3), 85 (5.0), 81 (35.3), 80 (4.0), 79 (26.0), 77 (19.8), 75 (7.4), 69 (7.33), 68 (13.5), 67 (68.6), 65 (12.0), 55 (21.6), 53 (14.7). HRMS. Found: 192.0477. Calcd. 192.0473 for $C_9H_{14}{}^{35}Cl_2$.

2-*exo*-Dichloromethyl-1-methylbicyclo[4.1.0]heptane (19). ^{1}H NMR (360 MHz) δ 6.09 (1H, d, $J = 3.6$ Hz); 2.31 (1H, dt, $J =$

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3.9, 8.8 Hz), 1.14 (3H, s), 0.85 (1H, m), 0.56 (1H, t, J = 5.4 Hz), 0.48 (1H, dd, J = 5.1, 9.0 Hz). ^{13}C NMR (90.6 MHz) δ 76.9, 50.3, 26.7, 24.2, 16.9. All others signals overlapped with those of **18**. MS (70 eV) *m*/*e* (%) 194, 192 ($M^{+\cdot}$, 0.81, 1.43), 159, 157 (1.2, 4.0), 145, 143 (1.2, 3.8), 122 (2.4), 121 (4.6), 115 (4.0), 110 (8.8), 109 (100), 105 (7.4), 103 (3.5), 102 (3.3), 101 (4.3), 95 (7.6), 93 (15.8), 91 (17.5), 88 (37.0), 85 (3.7), 83 (5.4), 82 (5.7), 81 (39.8), 79 (29.3), 77 (22.3), 75 (8.3), 68 (15.0), 67 (77.3), 65 (13.5), 55 (24.3), 53 (16.6).

1-Methylcyclopentene. It was prepared from 21.0 g of 1-methylcyclopentan-1-ol. 14.4 g was obtained. Yield: 95%. ^{1}H NMR (360 MHz) δ 5.3 (dd, 1H, J = 1.6, 3.5 Hz), 2.30−2.19 (m, 4H), 1.88−1.83 (m, 2H), 1.72 (s, 3H). ^{13}C NMR (90.6 MHz) δ 140.4 (s), 124.2 (d), 36.8 (t), 32.6 (t), 23.2 (t), 16.5 (q).

1-Methylbicyclo[3.1.0]hexane (20).[13a,87] ^{13}C NMR (90.6 MHz) δ 33.80 (t), 27.9 (t), 24.1 (d), 23.9 (s), 21.6 (q), 21.7 (t), 12.9 (t).

5-*exo*-Dichloromethyl-1-methylbicyclo[3.1.0]hexane (22). ^{1}H NMR (360 MHz) δ 0.34 (t, 1H, J = −4.8, 8.4 Hz), 0.45 (ddd, 1H, J = 1.0, 4.9, 7.8 Hz), 1.22 (s, 3H), 1.21−1.15 (m, 1H), 1.45−1.52 (m, 1H), 1.84−1.64 (m, 3H), 2.62 (m, 1H, J = 5.2, 8.2 Hz), 5.71 (d, J = 5.2 Hz). ^{13}C NMR (90.6 MHz) δ 77.8 (d), 53.4 (d), 32.4 (t), 27.2 (d), 26.2 (t), 25.2 (s), 29 (q), 14.7 (t). MS (70 eV) *m*/*e* (%) 180, 178 (M^+, 1.7, 2.7), 145, 143 (1.0, 2.3), 127 (1.1), 115 (1.1), 108 (1.2), 107 (14.5), 105 (1.6), 96 (7.5), 95 (100), 94 (1.4), 93 (7.1), 92 (1.5), 91 (9.9), 79 (8.6), 67 (7.8).

7,7-Dimethylbicyclo[4.1.0]heptane (23).[46b] Cuprous thiocyanate (1.22 g, 20 mmol) was placed in a flame-dried 50 mL two-necked flask, and dry ether (5 mL) was added. Methyllithium (18 mL, 20 mmol) was added to the suspension at −78 °C, and the mixture was gradually warmed to −10 °C over 30 min. Then the mixture was cooled to −20 °C, and a solution of 7,7-dibromonorcarane (1.27 g, 5 mmol) in dry ether (5 mL) and hexamethylphosphoric triamide (HMPT) (0.5 mL) was added to the mixture at the same temperature. The reaction mixture was stirred for 1.5 h, and methyl iodide (2 mL) was added at −50 °C. After 10 min the reaction mixture was quenched with saturated aqueous ammonium chloride at −50 °C and the precipitate was filtered on a Celite bed. The filtrate was extracted with ether and the organic layer was washed with 5% aqueous ammonia. 0.42 g was obtained. Yield: 75.5%. ^{1}H NMR (360 MHz) δ 1.87−1.78 (2H, m), 1.40−1.34 (2H, m), 1.28−1.13 (4H, m), 0.97 (3H, s), 0.95 (3H, s), 0.57−0.52 (2H, m). ^{13}C NMR (90.6 MHz) δ 29.4, 22.2, 19.2, 19.0, 17.1, 15.4.

2-Dichloromethyl-7,7-dimethylbicyclo[4.1.0]heptane (24a, 24b). Reaction of 7,7-dimethylnorcarane **23** with dichlorocarbene generated by ultrasonication. (Ultrasonic cleaner: Fisher, 100w/47 kHz, 3 d continuous). ^{1}H NMR (360 MHz) δ 5.83 (d, 1H, H−CCl_2, J = 4.7 Hz), 5.54 (d, J = 10.0 Hz, 1H, H−CCl_2), 2.55 (1H, m, 2-CH). ^{13}C NMR (90.6 MHz) δ 79.2, 78.2, 46.3, 43.3, 29.7, 28.8, 26.8, 25.4, 23.6, 23.4, 22.4, 22.2, 21.8, 19.4, 18.8, 18.3, 18.3, 17.8, 17.3, 15.8. IR (film) ν 2994, 2939, 2864, 1451, 1449, 1375, 1224, 1220, 1111, 864, 788, 755, 733, 694 cm^{-1}. MS (70 eV) *m*/*e* (%) 206 (M^+, 1), 135 (3), 124 (15), 123 (100), 95 (10), 93 (10), 91 (16), 81 (47), 79 (21), 67 (70). HRMS. Found: 206.0630. Calcd 206.0629 for $C_{10}H_{16}{}^{35}Cl_2$.

1-Methoxycyclopentene.[88] ^{1}H NMR (360 MHz) δ 4.41 (1H, s), 3.55 (3H, s), 2.28 (2H, m), 1.84 (2H, m), 1.7 (1H, m). ^{13}C NMR (90.6 MHz) δ 112.0 (s), 93.1 (d), 56.4 (q), 34.1 (t), 28.8 (t), 21.4 (t).

1-Methoxybicyclo[4.1.0]heptane (26).[47] ^{1}H NMR (360 MHz) δ 3.23 (s), 2.18−1.88 (3H, m), 1.47−1.37 (1H, m), 1.30−1.20 (1H, m), 1.18−1.12 (1H, m), 0.81 (ddd, J = 1.3, 5.2, 10.7 Hz), 0.22 (dd, J = 5.2, 6.2 Hz). ^{13}C NMR (90.6 MHz) δ 60.9 (s), 50.2 (q, J = 141 Hz), 27.0 (t, J = 125 Hz), 24.4 (t, J = 127 Hz), 21.8 (t, J = 128 Hz), 21.2 (t, J = 122 Hz), 18.6 (d, J = 160 Hz), 17.1 (t, J = 157 Hz).

1-Ethoxybicyclo[4.1.0]heptane (27).[47,48] ^{1}H NMR (360 MHz) δ 3.50 (1H, dq, J = 8.0, 7.1 Hz), 3.43 (1H, dq, J = 7.0, 8.9 Hz), 1.12 (3H, t, J = 7.5 Hz), 0.81 (1H, dd, J = 5.1, 10.8 Hz), 0.22 (dd, 1H, J = 5.3, 6.1 Hz). ^{13}C NMR (90.6 MHz) δ 61.2 (t, J = 137 Hz), 59.9 (s), 28.1 (t, J = 127 Hz), 24.5 (t, J = 128 Hz), 21.9 (t, J = 127 Hz), 21.3 (t, J = 129 Hz), 18.7 (d, J = 160 Hz), 17.3 (t, J = 158 Hz), 15.7 (d, J = 127 Hz). MS (70 eV) *m*/*e* (%) 140 (28), 125 (23), 112 (27), 97 (59), 86 (11), 83 (100), 55 (97).

1-(1′-Dichloromethylethoxy)bicyclo[4.1.0]heptane (28a, 28b). ^{1}H NMR (360 MHz) δ 5.78 (d, J = 3.2 Hz), 5.71 (d, J = 3.2 Hz), 4.06−3.98 (2H, m), 2.18−2.07 (2H, m), 2.04−1.94 (4H, m), 1.55−1.42 (2H, m), 1.40 (d, J = 14.5 Hz), 1.33 (3H, d, J = 10.4 Hz), 1.28−1.19 (6H, m), 1.15−1.03 (2H, m), 0.97 (2H, ddd), 0.31 (2H, dd, J = 5.5, 11.7 Hz). ^{13}C NMR (90.6 MHz) δ 76.9, 76.7 (d), 75.4, 75.2 (d), 61.4, 61.3 (s), 29.5 (t), 24.2 (t), 31.3 (t), 19.1,18.9 (d), 17.4, 17.3 (t), 16.2, 15.6 (q). IR (film) ν 3072, 2991, 2933, 2858, 1450, 1378, 1259, 1196, 1103, 1087, 1020, 966, 940, 883, 768, 706 cm^{-1}. MS (70 eV) *m*/*e* (%) major isomer: 222 (0.9), 187 (16), 151 (0.3), 112 (29), 97 (38), 95 (47), 83 (51), 55 (100). Minor isomer: 222 (1.5), 187 (19), 151 (0.4), 112 (30), 97 (38), 95 (47), 83 (51), 55 (100). HRMS. Found: 222.0574, Calcd. 222.0578 for $C_{10}H_{16}{}^{35}Cl_2$.

2-*endo*-Methoxybicyclo[3.1.0]hexane (29). ^{1}H NMR (360 MHz) δ 4.09 (1H, dt, J = 4.5, 7.7 Hz), 3.36 (3H, s), 1.88−1.81 (1H, m), 1.76−1.70 (2H, m), 1.50−1.45 (1H, m), 1.33−1.24 (1H, m), 1.11 (1H, tt, J = 9.7, 12.1 Hz), 0.54 (1H, "q", J = 4.1 Hz), 0.37 (1H, dt, J = 5.1, 7.8 Hz). ^{13}C NMR (90.6 MHz) δ 83.3 (d, J = 139 Hz), 57.0 (q, J = 140 Hz), 25.7 (t, J = 128 Hz), 25.1 (t, J = 129 Hz), 19.3 (d, J = 166 Hz), 16.3 (d, J = 168 Hz), 4.1 (t, J = 162 Hz).

2-*endo*-Methoxy-2-*exo*-dichloromethylbicyclo[3.1.0]hexane (30). To a 50 mL two-necked flask, equipped with argon inlet and refluxing condenser, were added freshly ground NaOH powder (5 g) and 15 mL of chloroform. It was followed with 515 mg (4.6 mmol) of 2-*endo*-methoxybicyclo[3.1.0]hexane (**29**) in 5 mL of chloroform, and 5 mg of TEBA. Then it was ultrasonicated for 5 h. Analytical GC monitored the progress of the reaction. After 5 h, it was filtered with the aid of Celite and evaporated to no solvent. The mixture was dissolved in the least amount of pentane necessary, and passed through a short column of silica gel to get rid of polychlorides. The filtrate was evaporated, 838 mg of a light yellowish oil was obtained. Yield: 94%. The analytical sample was obtained through preparative GC (column H). ^{1}H NMR (360 MHz) δ 5.93 (1H, s), 3.43 (3H, s), 2.11 (1H, dd, J = 9.3, 14.3 Hz), 1.98 (1H, dq, J = 4.4, 11.2 Hz), 1.80 (1H, dd, J = 8.7, 12.7 Hz), 1.55−1.40 (3H, m), 0.71 (1H, dt, J = 5.4, 7.9 Hz), 0.56 (1H, q, J = 4.2 Hz). ^{13}C NMR (90.6 MHz) δ 90.9 (s), 76.6 (d, J = 173 Hz), 53.2 (q, J = 142 Hz), 30.7 (t, J = 133 Hz), 26.7 (t, J = 131 Hz), 21.3 (d, J = 169 Hz), 18.8 (d, J = 169 Hz), 7.35 (t, J = 161 Hz). IR (film) ν 3074, 3036, 2942, 2831, 1458, 1340, 1221, 1118, 1030, 819 cm^{-1}. MS (70 eV) *m*/*e* (%) 155 (2.2), 153 (3.5), 112 (7.7), 111 (100), 91 (10.3), 85 (2.4), 83 (3.6), 79 (57.8), 75 (3.7), 67 (2.9), 65 (5.4), 57 (2.8), 55 (6.9), 51 (5.9). HRMS. Found: 159.0575. Calcd 159.0577 for $C_8H_{12}O^{35}Cl$.

2-*endo*-Methoxybicyclo[4.1.0]heptane (31).[49] ^{1}H NMR (360 MHz) δ 3.75 (1H, "q"), 3.35 (3H, s), 1.81−1.75 (1H, m), 1.60−1.50 (1H, m), 1.50−1.40 (1H, m), 1.40−1.30 (1H, m), 1.20−1.05 (4H, m), 0.51 (1H, dt), 0.28 (1H, "q"). ^{13}C NMR (90.6 MHz) δ 75.4, 55.2, 27.1, 23.4, 19.8, 13.7, 12.2, 7.0.

2-*endo*-Methoxy-2-*exo*-dichloromethylbicyclo[4.1.0]heptane (32). To a 50 mL two-necked flask, equipped with argon inlet and refluxing condenser, were added freshly ground NaOH powder (5 g) and 15 mL of chloroform. It was followed with 550 mg (4.6 mmol) of 2-*endo*-methoxybicyclo[4.1.0]heptane (**31**) in 5 mL of chloroform, and 5 mg of TEBA. Then it was ultrasonicated for 5 h. Analytical GC monitored the progress of the reaction. After 5 h, it was filtered with the aid of Celite and evaporated to no solvent. The mixture was dissolved in the least amount of pentane necessary, and passed through a short column of silica gel to get rid of

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polychlorides. The filtrate was evaporated, 879 mg of light yellowish oil was obtained. Yield: 96%. The analytical sample was obtained through preparative GC (column I). ^{1}H NMR (360 MHz) δ 5.97 (1H, s), 3.36 (3H, s), 1.86−1.83 (m, 1H), 1.72−1.58 (3H, m), 1.40 (1H, m), 1.27−1.18 (2H, m), 0.92 (1H, td, J = 5.5, 8.9 Hz), 0.71 (1H, td, J = 8.9, 4.9 Hz), 0.51 (1H, q, J = 5.4 Hz). ^{13}C NMR (90.6 MHz) δ 78.5 (s), 77.8 (d, J = 168 Hz), 49.8 (q), 28.4 (t, J = 127 Hz), 22.8 (t, J = 125 Hz), 15.6 (d, J = 157 Hz), 14.4 (t, J = 128 Hz), 12.6 (d, J = 162 Hz), 6.0 (t, J = 155 Hz). IR (film) ν 3073, 3005, 2941, 2856, 2826, 1468, 1449, 1433, 1386, 1221, 1158, 1111, 1093, 1078, 1057, 999, 953, 926, 904, 871, 836, 784, 762, 735 cm^{-1}. MS (70 eV) *m*/*e* (%) 173 (0.37), 141 (2.1), 126 (9.2), 125 (100), 105 (8.9), 97 (4.9), 95 (7.3), 93 (39.5), 91 (17.0), 85 (3.4), 83 (5.0), 79 (12.0), 78 (22.2), 71 (6.0), 67 (15.5), 65 (7.9), 57 (2.8), 55 (7.1), 53 (9.2). Anal. Calcd. for $C_9H_{14}OCl_2$: C, 51.69, H, 6.75. Found: C, 51.40, H, 6.71.

Bicyclo[5.1.0]octane (38).[83a] The title compound was prepared from cycloheptene by the general cyclopropanation procedure. Yield: 54%. ^{13}C NMR (90.6 MHz) δ 32.7, 31.1, 29.8, 14.8, 16.4.

2-*endo*-Dichloromethylbicyclo[5.1.0]octane (39a). The general procedure for dichlorocarbene insertion reactions was used. The reaction was performed with 0.53 g of **38**. After workup, 599 mg of yellowish oil were obtained. Yield: 65%. Ratio of **39a**:**39b** = 71:29. Separation of the two isomers was accomplished with preparative GC (column H). Purity: 96%. ^{1}H NMR (360 MHz) δ 5.91 (1H, d, J = 3.3 Hz), 2.28−2.21 (1H, m), 2.02−1.95 (2H, m), 1.82−1.74 (1H, m), 1.64 (2H, dq, J = 15.0, 3.1 Hz), 1.56−1.48 (1H, m), 1.43−1.32 (1H, m), 1.27−1.13 (1H, m), 1.01−0.74 (4H, m), 0.23 (1H, "q", J = 4.8 Hz). ^{13}C NMR (90.6 MHz) δ 78.7, 53.4, 31.7, 31.2, 30.8, 29.1, 17.9, 15.7, 15.1. IR (film) ν 3064, 2995, 2925, 2853, 1285, 1219, 1027, 926, 840, 805, 736, 680 cm^{-1}. MS (70 eV) *m*/*e* (%) 194, 192 (M^+, 0.5, 0.8) 159, 157 (2.5, 8.7), 130 (15), 121 (10), 109 (28), 93 (13), 91(11), 90 (10), 88 (31), 81 (48), 79 (31), 77 (18), 75 (11), 67 (100), 65 (13), 55 (23), 54 (15), 53 (17), 51 (10). HRMS. Found: 192.0477. Calcd 192.0472 for $C_9H_{14}Cl_2$.

2-*exo*-Dichloromethylbicyclo[5.1.0]octane (39b). Purity: 85%. ^{1}H NMR (360 MHz) δ 5.92 (1H, d, J = 2.7 Hz), 2.40 (1H, m), 0.95−0.83 (2H, m), 0.59 (1H, "q", J = 5.6 Hz), 0.41 (1H, "dt", J = 8.9, 5.5 Hz), other signals are not identifiable. ^{13}C NMR (90.6 MHz) δ 80.3, 49.2, 30.9, 29.1, 27.4, 25.6, 17.5, 15.6, 14.0. IR (film) ν 3077, 2991, 2914, 2857, 1463, 1444, 1291, 1224, 1086, 1072, 1019, 780, 756, 732, 708 cm^{-1}. MS (70 eV) *m*/*e* (%) 159, 157 ([M−Cl]$^+$, 1.8, 5.7), 130 (10), 109 (37), 88 (19), 79 (22), 77 (13), 67 (100), 65 (10), 55 (19), 53 (12). HRMS. Found: 192.0468. Calcd 192.0472 for $C_9H_{14}Cl_2$.

***cis*-1-(2′-Hydroxyethyl)-2-ethylcyclopropane.**[89] To a three-necked 250 mL flask equipped with a mechanical stirrer and a refluxing condenser were added under argon ether (20 mL), zinc powder (13 g, 0.2 mol, 7 μm) cuprous chloride powder (2.0 g, 0.002 mol), and dibromomethane (17.4 g, 0.1 mol). After ultrasonification and stirring for 0.5 h, the color of the mixture turned dark gray red. Alkene **40** (5.0 g, 0.05mol) in ether (15 mL) was added dropwise to the mixture over 0.5 h and continued to be ultrasonicated and stirred for an additional 6 h. Gas chromatography was used to monitor the progress of the reaction. The reaction mixture was filtered with the aid of Celite. The filtrate was washed with saturated ammonium chloride solution, brine, and dried over $MgSO_4$ over night. The filtrate was evaporated carefully through a Vigreux column and then distilled. A fractional distillation was done and the fraction of boiling point of 169−175 °C was collected, 6.53 g, yield: 75%. ^{1}H NMR (360 MHz) δ 3.64 (2H, t, J = 7.5 Hz), 2.68 (1H, s, OH), 1.67 (sextet, 1H, J = 6.4 Hz), 1.36 (2H, quintet, J = 6.4 Hz), 1.18 (1H, sextet, J = 6.5 Hz), 0.68 (2H, m_c), 0.58 (1H, m_c), −0.28 (1H, q, J = 5.3 Hz). ^{13}C NMR (90.6 MHz) δ 63.2 (t), 31.5 (t, J = 123 Hz), 21.9 (t, J = 123 Hz), 17.0 (d, J = 146 Hz), 14.2 (q, J = 124 Hz), 12.2 (d, J = 157 Hz), 10.2 (t, J = 160 Hz). IR (film) ν 3347, 3064, 2954, 1446, 1412, 1260, 1094, 1020, 803 cm^{-1}. MS (70 eV) *m*/*e* (%) 114 (M^+, 0.4), 96 ($M^{+\cdot}$-H_2O, 10.5), 95 (3.0), 82 (7.0), 81 (100), 79 (9.8), 69 (10.3), 68 (32.7), 67 (34.2), 57 (18.3), 56 (13.2), 55 (76.9), 54 (20.3), 53 (13.3), 41 (47.2).

***cis*-1-(2′-Tosylateethyl)-2-ethylcyclopropane.** To a solution of 2.02 g of *cis*-1-(2′-hydroxyethyl)-2-ethylcyclopropane (17.7 mmol) in 100 mL of $CHCl_3$, 4.30 g of ρ-toluenesulfonyl chloride (22.5 mmol) and 5 mL of pyridine (4.0 g, 50 mmol) were added, at a temperature of 0−5 °C, and stirred under argon overnight. The progress of the reaction was monitored with TLC (solvent: hexanes: chloroform 3:2). After the reaction was completed, the reaction mixture was poured into a mixture of ice and HCl. Then it was extracted with $CHCl_3$, washed two times with water, and dried over $MgSO_4$. The drying agent was filtered off and the filtrate was evaporated in vacuo using a Rotavapor. 4.39 g of the tosylate (**40b**) was obtained as a faint yellow oily liquid. Yield: 90%. ^{1}H NMR (360 MHz) δ 7.79 (2H, d, J = 8.3 Hz), 7.33 (2H, J = 8.0 Hz), 4.08 (2H, t, J = 7.1 Hz), 2.43 (3H, s), 1.75 (1H, sextet, J = 6.9 Hz), 1.51 (1H, septet, J = 7.2 Hz), 0.93 (3H, t, J = 7.3 Hz) 0.69−0.62 (2H, m), 0.55 (1H, dt, J = 4.6, 7.6 Hz), −0.30 (1H, "q"). ^{13}C NMR (90.6 MHz) δ 144.5, 133.3, 129.7, 127.8, 70.9, 28.0, 21.8, 21.5, 17.3, 14.1, 11.7, 10.3. IR (film) ν 3064, 2960, 1596, 1493, 1454, 1359, 1176, 815, 778 cm^{-1}. MS (70 eV) *m*/*e* (%) 155 (32.4), 96 (54.7), 81 (100), 68 (36), 67 (47), 65 (39), 55 (49), 54 (88).

***cis*-1,2-Diethylcyclopropane (41)**.[51b,c,52a] In a 100 mL two-necked round bottomed flask equipped with a condenser *cis*-1-(2′-tosylateethyl)-2-ethylcyclopropane (0.2 g, 25 mmol) and lithium aluminum hydride (0.05 g, 1.3 mmol) were added in 10 mL of ether. Ultrasonicated for 2 h the gray reaction mixture was poured slowly into an ice bath. The mixture was extracted with ether, washed with brine, and dried over $MgSO_4$ overnight. The drying agent was then filtered off and the filtrate was distilled. The boiling point of the product was 93.5 °C, yield: 0.056 g (76%) ^{1}H NMR (360 MHz) δ 1.38 (2H, septet), 1.22 (2H, septet), 0.98 (6H, t, J = 7.2 Hz), 0.68−0.62 (2H, m), 0.56 (1H, dt), −0,33 (1H, q). ^{13}C NMR (90.6 MHz) δ 21.8 (t, J = 128 Hz), 17.9 (d, J = 158 Hz), 14.5 (q, J = 125 Hz), 10.5 (d, J = 160 Hz). MS (70 eV) *m*/*e* (%) 98 (M^+, 19.7), 69 ($M^{+\cdot}$-CH_2CH_3), 60.6), 56 (96.8), 55 (70.2), 42 (25), 41 (100).

***cis*-1-(2,2-Dichloro-1-methylethyl)-2-ethylcyclopropane (42a**, **42b)**. To a two-necked 50 mL round-bottomed flask, equipped with a condenser and connected to an argon outlet, were added ground NaOH (3.0 g, 0.075mol), compound **41** (0.5 g, 0.0051mol), TEBA and 10 mL of $CHCl_3$. The brown reaction mixture was ultrasonicated for 6 h. The progress of the reaction was monitored by gas chromatography. The solution was washed with ether and then filtered with the aid of Celite. The filtrate was extracted with water and dried over $MgSO_4$. After removal of the drying agent the filtrate was filtered again and evaporated in vacuo using a Rotavapor. The product shows two isomers (ratio 3:2), 0.28 g, yield: 30%. The separation of the isomers was achieved on column F. Major isomer: ^{1}H NMR (360 MHz) δ 5.92 (1H, d, J = 3.2 Hz), 1.68−1.61 (1H, m), 1.58−1.52 (1H, m), 1.24 (3H, d, J = 6.5 Hz), 1.01 (4H, m), 0.84−0.78 (2H, m), 0.70 (1H, dt, J = 4.5, 7.7 Hz), −0.11 (1H, "q", J = 5.5 Hz). ^{13}C NMR (90.6 MHz) δ 79.5, 44.4, 21.9, 20.2, 17.8, 14.3, 14.3, 10.0. IR (film) ν 3067, 2957, 2919, 2873, 1455, 1379, 1314, 1263, 1217, 1111, 1090, 1065, 1024, 890, 815, 726 cm^{-1}. MS (70 eV) *m*/*e* (%) 154 (0.3), 151 (0.5), 147 (0.9), 146 (0.6), 145 (3.1), 109 (17), 97 (60), 89 (15), 77 (12), 76 (14), 75 (12), 69 (24), 68 (14), 67 (20), 66 (10), 55 (100), 53 (17). HRMS. Found: 145.0784. Calcd 145.0784 for $C_8H_{14}{}^{35}Cl$. Minor isomer: ^{1}H NMR (360 MHz) δ 5.91 (1H, d, J = 2.7 Hz), 1.71 (3H, m), 1.25 (3H, d, J = 9.0 Hz), 1.03 (3H, m), 0.85−0.77 (2H, m), 0.74 (1H, dt, J = 4.1, 10.3 Hz), −0.18 (1H, "q", J = 4.2 Hz). ^{13}C NMR (90.6 MHz) δ 78.6, 44.2, 22.3, 20.2, 18.8, 14.3, 14.1, 10.0. IR (film) ν 3062, 2961, 2931, 2861, 1590, 1455, 1379, 1219, 1153, 1038, 887, 846, 781, 755 cm^{-1}. MS (70 eV) *m*/*e* (%) 147 (0.3), 146 (0.4), 145 (1.2), 144 (1.1), 109 (11), 104 (15), 98 (4.2), 97 (50.5), 89

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(11), 76 (15), 69 (22), 68 (17), 67 (14), 55 (100), 53 (12). HRMS. Found: 180.0475. Calcd 180.0473 for $C_8H_{14}{}^{35}Cl_2$.

***trans*-1-(2′-Hydroxyethyl)-2-ethylcyclopropane.**[89] To a two-necked flask were added 5.0 g of 3-*trans*-hexen-1-ol (**43**), 20 g (114 mmol) of dibromomethane, 13 g (0.198 mmol) of Zn powder, and 2.4 g (24 mmol) of CuCl, and the mixture was ultrasonicated for 4 h. After workup, 4.94 g were obtained. Yield: 86%. ^{1}H NMR (360 MHz) δ 3.67 (2H, t, J = 6.5 Hz), 1.57 (1H, s), 1.45 (2H, m), 1.24 (2H, m), 0.93 (3H, t, J = 7.2 Hz), 0.43 (2H, m), 0.21 (2H, t, J = 6.7 Hz). ^{13}C NMR (90.6 MHz) δ 63.2 (t, J = 156 Hz), 37.2 (t, J = 126 Hz), 27.1 (t, J = 126 Hz), 20.3 (d, J = 156 Hz), 14.9 (d, J = 150 Hz), 13.6 (q, J = 125 Hz), 11.1 (t, J = 162 Hz). IR (film) ν 3349, 3066, 2960, 2924, 1453, 1041, 1011, 940, 877 cm^{-1}. MS (70 eV) *m*/*e* (%) 114 (M^+, 0.4), 99 (1.2), 96 (7.5), 81 (70), 69 (11), 68 (30), 67 (34), 57 (22), 56 (16), 55 (100), 54 (26), 53 (14). HRMS. Found: 114.1046. Calcd. 114.1045 for $C_7H_{14}O$.

***trans*-1-(2′-Toluenesulfonylethyl)-2-ethylcyclopropane.** To the solution of 1.14 g (10 mmol) of *trans*-1-(2′-hydroxyethyl)-2-ethylcyclopropane in 25 mL of chloroform were added 1.71 g (9 mmol) of *p*-toluenesulfonyl chloride and 1 mL (0.94 g, 12 mmol) of pyridine at 0−5 °C and stirred under argon overnight. The progress of the reaction mixture was monitored by TLC (hexane: chloroform 3:2). After the reaction was complete, the reaction was poured into a mixture of ice and conc. hydrochloric acid. Then the reaction mixture was extracted with chloroform, and the organic layers were washed two times with water, and dried over $MgSO_4$. After removal of the drying agent, the filtrate was evaporated in vacuo using a Rotavapor. The tosylate was obtained as a faint yellow oil. Yield: 2.25 g (84%). ^{1}H NMR (360 MHz) δ 7.78 (2H, d, J = 8.3 Hz), 7.32 (2H, d, J = 8.6 Hz), 4.05 (2H, t, J = 6.5 Hz), 2.43 (3H, s), 1.58−1.50 (2H, m), 1.20−1.10 (2H, m), 0.87 (3H, t, J = 7.3 Hz), 0.43−0.35 (2H, m), 0.19−0.11 (2H, m). ^{13}C NMR (90.6 MHz) δ 144.6 (s), 133.5 (s), 129.7 (d, J = 160 Hz), 127.9 (d, J = 166 Hz), 70.6 (t, J = 149 Hz), 33.5 (t, J = 125 Hz), 26.8 (t, J = 123 Hz), 21.6 (q, J = 127 Hz), 21.4 (d, J = 158 Hz), 14.4 (d, J = 160 Hz), 11.2 (t, J = 160 Hz). IR (film) ν 3063, 2959, 2926, 2871, 1598, 1495, 1461, 1360, 1306, 1291, 1188, 1177, 1097, 1020, 965, 942, 908, 815, 765, 735, 664 cm^{-1}. MS (70 eV) *m*/*e* (%) 173 ([M−C_7H_{12}]$^+$, 7), 155 (31), 97 (5), 96 (68), 91 (70), 81 (100), 68 (43), 65 (30), 55 (54), 54 (75).

***trans*-1,2-Diethylcyclopropane (44)**.[51b,c,52a] To a two-necked flask equipped with reflux condenser and an argon inlet were added 0.57 g (15 mmol) of $LiAlH_4$ and 15 mL of ether. Then the tosylate (1.5 g, 5.6 mmol) in 5 mL of ether was added dropwise. The reaction was kept stirring at room temperature for an additional 1 h. TLC was used to monitor the reaction (hexane:acetone 5:1) until the disappearance of the starting material. The reaction mixture was poured into crushed ice and then extracted with ether and dried over $MgSO_4$. After removal of the drying agent, the filtrate was distilled through a Vigreux column (bp 98−102 °C). Yield: 0.23 g (42%). The analytical sample and the sample for the dichlorocarbene insertion reaction were obtained by prep. GC (column I). ^{1}H NMR (360 MHz) δ 1.27 (2H, septet, J = 7.3 Hz), 1.12 (2H, septet, J = 7.3 Hz), 0.93 (6H, t, J = 7.3 Hz), 0.40−0.33 (2H, m), 0.14 (2H, t, J = 6.8 Hz). ^{13}C NMR (90.6 MHz) δ 27.3 (t, J = 123 Hz), 20.5 (d, J = 159 Hz), 13.7 (q, J = 124 Hz), 11.4 (t, J = 163 Hz).

***trans*-1-(2,2-Dichloro-1-methylethyl)-2-ethylcyclopropane (45a, 45b)**. The general procedure for dichlorocarbene insertion reactions was used. The reaction was performed with 0.5 g (5.1 mmol) of **44** (reaction time 5 h). The product shows two stereoisomers (ratio 1.3:1), 0.27 g, yield 29%. The separation of the isomers was achieved on column H. Major isomer, purity 86%: ^{1}H NMR (360 MHz) δ 5.88 (1H, d, J = 2.9 Hz), 1.43−1.33 (2H, m), 1.15−1.07 (1H, m), 1.22 (3H, d, J = 6.4 Hz), 0.95 (3H, t, J = 7.3 Hz), 0.54−0.48 (2H, m), 0.42−0.37 (1H, m), 0.35−0.30 (1H, m). ^{13}C NMR (90.6 MHz) δ 78.7, 49.3, 26.8, 22.1, 20.6, 13.9, 13.6, 11.4. IR (film) ν 3061, 1452, 1377, 1249, 1219, 1073, 1066, 914, 892, 816, 733 cm^{-1}. MS (70 eV) *m*/*e* (%) 147, 145 ([M−Cl]$^+$, 0.2, 0.7), 146, 144 (0.3, 0.9), 130 (0.2), 97 (38), 76 (14), 55 (100). HRMS. Found: 180.0477. Calcd 180.0473 for $C_8H_{14}{}^{35}Cl_2$. Minor isomer, purity 97%: ^{1}H NMR (360 MHz) δ 5.89 (1H, d, J = 2.9 Hz), 1.39−1.29 (2H, m), 1.23−1.09 (1H, m), 1.19 (3H, d, J = 6.6 Hz), 0.96 (3H, t, J = 7.3 Hz), 0.65−0.50 (2H, m), 0.36−0.26 (2H, m). ^{13}C NMR (90.6 MHz) δ 78.8, 49.2, 26.8, 22.1, 20.6, 13.8, 13.6, 10.8. IR (film) ν 3062, 2961, 2911, 2871, 1455, 1374, 1314, 1219, 1022, 882, 841, 801, 736, 696 cm^{-1}. MS (70 eV) *m*/*e* (%) 146, 144 ([M−HCl]$^+$, 0.3, 0.6), 104 (12), 97 (319, 76 (14), 69 (18), 55 (100). HRMS. Found: 180.0470. Calcd 180.0473 for $C_8H_{14}{}^{35}Cl_2$.

An Improved Synthesis of *cis*-Bicyclo[4.2.0]octane (52). *(1) cis-1,2-Dihydroxymethylcyclohexane (**49**).*[56a] *cis*-1,2-Cyclohexanedicarboxyclic acid anhydride (**48**; 9.2 g, 60 mmol) in THF (100 mL) was added dropwise to a suspension of $LiAlH_4$ (5 g, 132 mmol) in THF (60 mL) stirred under argon. Stirring was continued 0.5 h at room temperature and 3 h at reflux. The mixture was cooled to room temperature. Wet ether (100 mL) and then Celite (10 g) were added. Water was added dropwise slowly until hydrogen development stopped. The mixture was filtered and the residue washed with ether. After removal of the solvent, the concentrated oil (7.9 g, 91%) was used directly for the next step without further purification. ^{1}H NMR (360 MHz) δ 4.32 (s, 2H), 3.56−3.66 (m, 2H), 3.38−3.48 (m, 2H), 1.77−1.87 (m, 2H), 1.20−1.56 (m, 8H). ^{13}C NMR (90.6 MHz) δ 63.6 (t, J = 140 Hz), 39.7 (d, J = 125 Hz), 26.9 (t, J = 127 Hz), 23.8 (t, J = 128 Hz).

*(2) cis-Cyclohexane-1,2-diyldimethyl ditosylate (**50**).*[56a] The diol (3.5 g, 24.2 mmol) in anhydrous pyridine (15 mL) was stirred in an ice−water bath while *p*-toluenesulfonyl chloride (11.5 g, 60 mmol) in pyridine (25 mL) was added dropwise. Stirring was continued at room temperature for 1 h, and then the mixture was allowed to stand overnight. The mixture was poured onto crushed ice to afford a solid which was filtered off and recrystallized from methanol (6.8 g, 63%), mp 78 − 79 °C. ^{1}H NMR (360 MHz) d 7.73 (d, 4H, J = 8.1 Hz), 7.33 (d, 4H, J = 8.1 Hz), 3.87 (d, 4H, J = 6.8 Hz), 2.43 (s, 6H), 1.90−2.10 (m, 2H), 1.25−1.45 (m, 8H). ^{13}C NMR (90.6 M Hz) δ 144.8, 132.6, 129.8 (d, J = 162 Hz), 127.7 (d, J = 168 Hz), 70.2 (t, J = 147 Hz), 36.4 (d, J = 126 Hz), 25.6 (t, J = 128 Hz), 22.7 (t, J = 129 Hz), 21.5 (q, J = 127.3 Hz).

*(3) cis-1,2-Diiodomethylcyclohexane (**51**).*[56a] A mixture of the ditosylate **50** (6.6 g, 14.6 mmol), powdered potassium iodide (24 g, 146 mmol), acetonitrile (40 mL), and polyethylene glycol 400 (0.2 g) was immersed in the water bath of an ultrasonic cleaner (33 kHz, 120 W) and was ultrasonicated for 1 h. Then the mixture was stirred under reflux overnight. Filtration to remove the inorganic substance afforded a colorless oil (4.8 g, yield: 90.4%). ^{1}H NMR (360 MHz) δ 3.05−3.18 (m, 4H), 2.00−2.10 (m, 2H), 1.51−1.67 (m, 4H), 1.38−1.51 (m, 2H), 1.24−1.36 (m, 2H). ^{13}C NMR (90.6 MHz) δ 42.0 (d, J = 130 Hz), 29.1 (t, J = 128 Hz), 22.8 (t, J = 125 Hz), 8.33 (t, J = 150 Hz).

*(4) cis-Bicyclo[4.2.0]octane (**52**).*[56c] A mixture of the diiodide (2.9 g, 8 mmol) and lithium (0.6 g, 86 mmol) in THF (30 mL) was ultrasonicated for 30 min. After filtration to remove the excess lithium, the product was separated on column D by preparative gas chromatography (0.82 g, 93%). ^{1}H NMR (360 MHz) δ 2.20−2.40 (m, 2H), 1.78−1.93 (m, 2H), 1.65−1.78 (m, 2H), 1.55−1.65 (m, 2H), 1.43−1.55 (m, 2H), 1.33−1.55 (m, 2H), 1.20−1.33 (m, 2H). ^{13}C NMR (90.6 MHz) δ 33.2 (d), 28.1 (t), 24.6 (t), 22.9 (t).

***cis*-1-Dichloromethylbicyclo[4.2.0]octane (53)**. (PGC separation on column E). ^{1}H NMR (360 MHz) δ 5.58 (s, 1H), 2.45 (m, 1H), 2.12−2.30 (m, 1H), 1.35−1.90 (m, 11H). ^{13}C NMR (90.6 MHz) δ 82.3 (d, J = 177 Hz), 46.6 (s), 37.3 (d, J = 134 Hz), 30.0 (t, J = 138 Hz), 28.3 (t, J = 128 Hz, *C*2), 25.9 (t, J = 126 Hz), 22.2 (t, J = 128 Hz), 20.8 (t, J = 126 Hz), 18.1 (t, J = 137 Hz). IR (film) ν 2940, 2860, 1450, 1288, 1228, 1215, 965, 920, 882, 800, 770, 720 cm^{-1}. MS (70 eV) *m*/*e* (%) 192, 194 ($M^{+\cdot}$, 0.5, 0.3), 164, 166, 168 (18, 12, 2), 157, 159 (7, 2), 129, 131 (84, 26), 121 (36), 109 (100), 93 (47), 91 (25), 81 (99.7], 79 (43), 77 (29), 67 (67), 65 (19), 55 (15), 54 (11), 53 (19), 51 (13), 41 (30), 39 (26). Anal. Calcd for $C_9H_{14}Cl_2$: C, 55.98; H, 7.31. Found: C, 55.74; H, 7.29.

***trans*-Cyclohexane-1,2-dimethanol (55)**.[90] ^{1}H NMR (360 MHz) δ 3.65−3.53 (4H, m), 2.95 (2H, s), 1.80−1.70 (2H, m), 1.66−1.60 (2H, m), 1.38−1.30 (2H, m), 1.28−1.18 (2H, m), 1.10−1.02 (2H, m). ^{13}C NMR (90.6 MHz) δ 67.8 (t, J = 140 Hz), 44.7 (d, J = 140 Hz), 29.8 (t, J = 127 Hz), 26.1 (t, J = 121 Hz).

***trans*-1,2-Diiodomethylcyclohexane (56)**.[57] ^{1}H NMR (360 MHz) δ 3.34−3.23 (4H, m), 1.80−1.72 (2H, m), 1.70−1.63 (2H, m), 1.41−1.30 (4H, m), 0.95−0.85 (2H, m). ^{13}C NMR (90.6 MHz) δ 41.3 (d, J = 125 Hz), 32.7 (t, J = 126 Hz), 25.5 (t, J = 127 Hz), 15.5 (t, J = 149 Hz).

***trans*-Bicyclo[4.2.0]octane (57)**.[56] ^{1}H NMR (360 MHz) δ 1.82−1.92 (1H, m), 1.64−1.74 (2H, m), 1.54−1.58 (2H, m), 1.40−1.48 (2H, m), 1.18−1-31 (2H, m). ^{13}C NMR (90.6 MHz) δ 45.5 (d, J = 131 Hz), 31.8 (t, J = 126 Hz), 29.4 (t, J = 134 Hz), 26.5 (t, J = 125 Hz).

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all new compounds, plus spectrometers, instrumentations, and PGC columns used. This material is available free of charge via the Internet at http://pubs.acs.org.

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