The Stereospecific Intramolecular Insertion of the Cyclopropylidenes Produced in the Reaction of *cis*- and *trans*-3-*tert*-Butyl-7,7-dibromobicyclo[4.1.0]heptane with Methyllithium[1]

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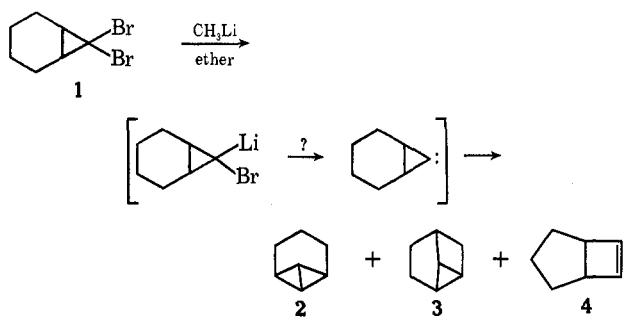
Addition of dibromocarbene to 4-*tert*-butylcyclohexene gives a mixture of 57% *cis*- and 43% *trans*-3-*tert*-butyl-7,7-dibromobicyclo[4.1.0]heptane (**7**). The treatment of *cis*-**7** with methyllithium leads to an intramolecular carbenoid insertion reaction which gives products (**9**, **11**, **12**) which are different from the products (**8**, **10**, **13**) obtained from *trans*-**7**. This result establishes that the stereoisomeric cyclopropylidene intermediates derived from *cis*- and *trans*-**7** do not interconvert and precludes the possibility of reversible opening of the cyclopropylidenes to 5-*tert*-butyl-1,2-cycloheptadiene. The six-membered ring of each cyclopropylidene must assume a half-chair conformation in which the *tert*-butyl group is equatorial. This conformation leads to selective insertion into either of the two axial C–H bonds which are cis to the carbenoid atom of the cyclopropylidene. The selectivity which is observed indicates that a tertiary C–H bond is substantially more reactive than a stereochemically comparable secondary C–H bond.

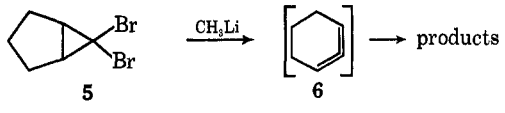
Many lines of recent evidence indicate that gem dihalides react with organolithium reagents to produce carbenoid intermediates which subsequently undergo a variety of reactions.[3] *gem*-Dibromocyclopropanes represent one of the more useful types of dihalides which serve as precursors for carbenoid intermediates. Thus, most *gem*-dibromocyclopropanes react with methyllithium to afford allenes in excellent yields,[4,5] either directly from an α-bromocyclopropyllithium intermediate or from rearrangement of the cyclopropylidene which would be derived from the former by loss of lithium bromide. In those cases where allenes are formed, no carbene or carbenoid intermediates have been trapped intermolecularly by olefins,[6] but Skattebøl[7] has reported the successful intramolecular trapping of several such intermediates with the formation of a number of interesting spiropentanes (tricyclic compounds).

In the systems which would lead to a highly strained allene, products derived from the carbene or carbenoid intermediates are found. Thus we have shown that the reaction of 7,7-dibromobicyclo[4.1.0]heptane (**1**) with methyllithium yields a variety of products which are indicative of a carbene or carbenoid intermediate.[4a,8] The mixture of the three hydrocarbons **2**, **3**, and **4** which result from intramolecular insertion can be obtained in 40–50% yield.[9] In addition, insertion on



the solvent, formation of a (formal) dimer of the cyclopropylidene, and trapping of the intermediate(s) with olefins to form spiropentanes stereospecifically all point toward the intermediacy of a carbene or carbenoid intermediate.[4a,8]

Although the products obtained from 7,7-dibromobicyclo[4.1.0]heptane clearly must have been derived from a carbene or carbenoid, it appeared to us that in small cyclic systems the cyclopropylidene and strained allene might interconvert. Marquis and Gardner[10] have found that 8,8-dibromobicyclo[5.1.0]octane reacts with methyllithium to give 1,2-cyclooctadiene and its dimer as well as carbene insertion products. In this case the strain in the cyclic allene presumably has diminished to the point where its formation is not prohibitive. Since 1,2-cycloheptadiene must be much more highly strained than 1,2-cyclooctadiene, intervention of the seven-membered-ring allene in reactions of 7,7-dibromobicyclo[4.1.0]heptane may seem out of the question, but we have found that 6,6-dibromobicyclo[3.1.0]hexane (**5**) reacts with methyllithium to give *exclusively 1,2-cyclohexadiene* (**6**), which subsequently leads to dimers and tetramers.[11] With this fact in mind, it seemed entirely possible that cyclopropylidene–allene *interconversion* might occur prior



(1) Acknowledgment is made to the donors of the Petroleum Research Fund Administered by the American Chemical Society (1549-A4) and to the National Science Foundation (GP1306) for support of this research.

(2) National Institutes of Health Predoctoral Fellow, 1962–1965.

(3) (a) G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967); (b) W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim/Bergstr., Germany, 1969.

(4) (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b), W. R. Moore and H. R. Ward, *ibid.*, **27**, 4179 (1962); (c) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961).

(5) Tetrasubstituted *gem*-dibromocyclopropanes are exceptions; intramolecular insertion products are formed. (a) W. R. Moore, K. Grant Taylor, P. Müller, Stan S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970); (b) L. Skattebøl, *ibid.*, 2361 (1970); (c) W. R. Moore and J. B. Hill, *ibid.*, 4343 (1970).

(6) (a) 2,2-Diphenylcyclopropylidene has been trapped with olefins in the base-catalyzed decomposition of nitrosourea and urethane precursors of 2,2-diphenyldiazomethane: W. M. Jones, *J. Amer. Chem. Soc.*, **82**, 6200 (1960), and subsequent papers in this series. (b) Treatment of 2,2-dibromo-1,1-diphenylcyclopropane with methyllithium, a reaction which must involve the related carbenoid, is reported[4c] to give only 1,1-diphenylallene; no olefin trapping products were detected.

(7) L. Skattebøl, *J. Org. Chem.*, **31**, 2789 (1966).

(8) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(9) A typical product ratio of **2**:**3**:**4** is ~96:4:3. The formation of compound **4** and related compounds in other systems (always minor) is significant in defining the mechanism of insertion; see ref 28.

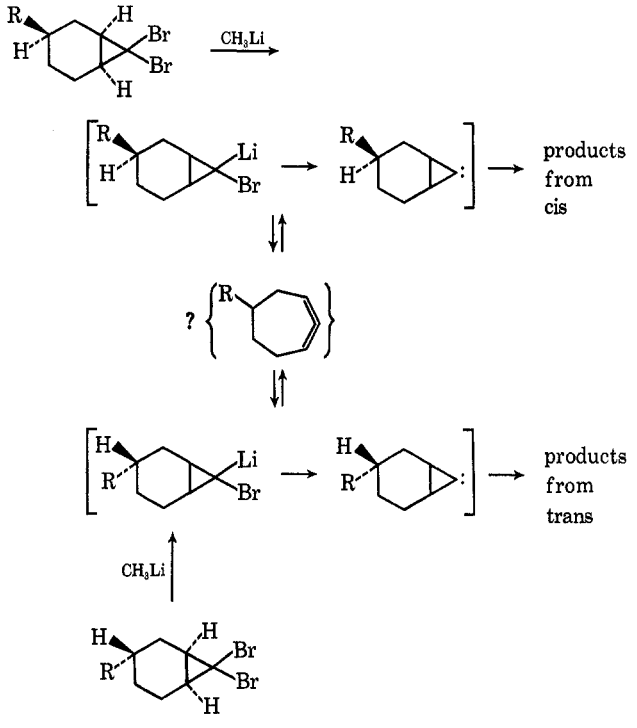
(10) E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966).

(11) W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, **92**, 5469 (1970).

to formation of the products from bicyclo[4.1.0]-heptylidene-7.

To examine this point, we elected to study the reactions of the cis and trans isomers of a 3-alkyl-7,7-dibromobicyclo[4.1.0]heptane. The principle is embodied in Scheme I. In the event that crossover

SCHEME I[a]



[a] All species are *dl*, only one enantiomer is shown.

products were observed, passage through a 1,2-cycloheptadiene would appear probable. At the outset, one must ask would failure to observe crossover products prove that a 1,2-cycloheptadiene was not an intermediate? On the basis of the arguments which follow, we believe that the answer to this question is clearly yes.

Three structural possibilities exist for 1,2-cycloheptadiene. (1) The diene could be described as being a "normal" (orthogonal) albeit highly strained allene. In this case the allene linkage would be somewhat twisted and bent and the other C–C–C bond angles would be distorted toward larger than normal values, all in the sense one finds upon constructing a simple model.[12] (2) The allene linkage could be planar with the three carbon atoms in that linkage still colinear. (3) The allene linkage could be planar and bent (nonlinear). In this case the structure would be similar to that proposed for 1,2-cyclohexadiene[11,13] and would resemble a 3-cycloheptenyl radical minus the C-2 hydrogen atom.[14]

In our system, the 3 substituent on the bicyclo-[4.1.0]heptane ring is *tert*-butyl, a bulky group which will be equatorial in the starting dibromides and carbene or carbenoid species derived from them. Each of the possible structures for 1,2-cycloheptadiene referred to above can exist in conformations which have clearly differentiated axial and equatorial positions at C-5 (equivalent to the C-3 positions of the reactants). Irrespective of the mechanism of ring opening, if a 1,2-cycloheptadiene is formed, the formation of the seven-membered ring can occur in a way which will retain the *tert*-butyl group in an equatorial conformation. Such a process must correspond to the lowest energy pathway; hence, it appears certain that it would be followed to a predominant extent. This line of reasoning leads to the conclusion that, if an allene intermediate were to be formed, both cis and trans bicyclic reactants would lead to the same equatorial 5-*tert*-butyl-1,2-cycloheptadiene which upon regenerating a cyclopropylidene would have to lead to crossover products.[15]

Results

The addition of dibromocarbene to a 4-alkylcyclohexene gives a mixture of the *cis*- and *trans*-3-alkyl-7,7-dibromobicyclo[4.1.0]heptanes in good yield, but the separation of the cis and trans isomers proved to be a major problem that dictated the course of the investigation. Thus 3-methyl-7,7-dibromobicyclo[4.1.0]-heptane appeared to be a single compound on more than 20 different (packed) glc columns; no separation was ever realized. Yet, reduction of the dibromide with sodium in liquid ammonia gave 3-methylbicyclo-[4.1.0]heptane which capillary glc showed was a 43:57 mixture of the cis and trans isomers (the stereochemistry was not assigned). Since the reduction would not affect the configuration of the C-3 methyl group, the dibromide must have been a similar mixture of isomers. Several other systems were examined, but only 3-*tert*-butyl-7,7-dibromobicyclo[4.1.0]heptane (**7**) proved to be suitable for this study. Dibromide **7**, obtained in 63% yield, could be partially resolved into the cis and trans isomers on 6 of 23 glc columns tried, the best giving a separation factor of only 1.04. Both glc and nmr analysis indicated a 43:57 ratio of isomers. Subsequent results established that the cis isomer predominated.[16] The slight preference for formation of the cis isomer must reflect subtle differences (not obvious) in steric hindrance of approach of dibromocarbene to the double bond.

Treatment of **7**[17] with methyllithium in ether at 0° gave a 62–66% yield of a mixture of isomeric hydrocarbons ($C_{11}H_{18}$) which were isolated by glc and shown to be the compounds indicated in Scheme II. All of the spectral properties of these compounds are in accord with the assigned structures.[18] Bicyclopentanes **10** and **11** show complex nmr patterns and infrared absorption in the C–H stretching region similar

(12) Framework Molecular Models, Prentice-Hall, Englewood Cliffs, N. J., probably give a representation as accurate as any.

(13) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

(14) While in principle these different possibilities exist for the structure of 1,2-cycloheptadiene, it clearly would be unreasonable to propose that the cis and trans systems could open to different types of allenes which did not interconvert.

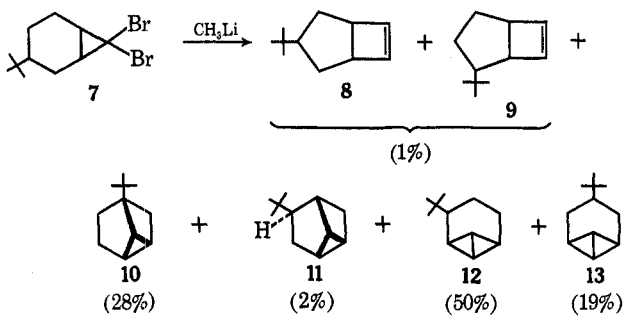
(15) A cis 3(*R*) and a trans 3(*R*) dibromide would lead to a common 5(*R*)-substituted 1,2-cycloheptadiene which subsequently could return to both cis and trans 5(*R*) bicyclic intermediates. It is immaterial whether or not return to one isomer (*e.g.*, *trans*) were favored, common products would be observed. It should be noted that this interconversion of cis and trans intermediates does not mean that the configuration at C-3 would be affected. If one were employing optically active reactants, even if crossover occurred, the products would be optically active.

(16) Reduction of **7** with sodium in liquid ammonia gave 3-*tert*-butylbicyclo[4.1.0]heptane. Although this material was not resolved on several glc columns, its nmr spectrum showed that it was also a mixture of isomers.

(17) All product isolation and identification was performed with the mixture of isomers.

(18) Full spectral data are given in the Experimental Section.

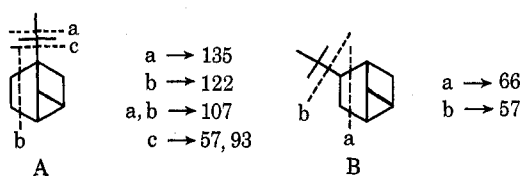
SCHEME II[a]



[a] Compounds are shown in order of increasing glc retention times.

to the spectra of **3**, and bicyclobutanes **12** and **13** show nmr signals and infrared absorption in the C–H stretching region similar to the spectra of **2**.

The mass spectra of **10** and **11** are strikingly different and are sufficient to define the structures (if not the stereochemistry of **11**). Thus **10** shows a fairly rich pattern which includes major peaks at *m/e* 57, 93 (base peak), 107, and 135 and a weak but significant peak at *m/e* 122, all of which can be readily accommodated by the fragmentations shown in structure A followed by straightforward rearrangements. In contrast, compound **11** shows a base peak at *m/e* 66, a major peak at *m/e* 57, and little else, a pattern which is clearly accounted for by the fragmentations shown in structure B.



The mass spectra of **12** and **13** are quite similar, showing dominant base peaks at *m/e* 57, but one significant difference is sufficient to distinguish between the 3 and 4 positions for the *tert*-butyl group. The molecular ion of **13** represents 2.90% of the sum of the intensities of all ions compared to only 1.33% for the molecular ion of **12**. Formation of a *tert*-butyl cation (*m/e* 57) clearly must be favored with the group in the 3 position, where bond cleavage will be directly facilitated by opening of the bicyclobutane ring.

Chemical evidence for the assignment of structures to **10**, **11**, **12**, and **13** as well as some transformations of these compounds appear in an accompanying paper.[19]

Compounds **8** and **9** emerged from the glc column ahead of the other compounds as two partially resolved peaks. Since these products were formed in such small amounts they were not extensively investigated, but, based on spectral data obtained on the mixture, it is clear that these peaks represent the 2- and 3-*tert*-butyl derivatives of **4**. Subsequent results indicate that **8** must have the *tert*-butyl group in the 3 position while **9** has a 2-*tert*-butyl group.[20]

In addition to the $C_{11}H_{18}$ hydrocarbons, higher boiling materials (much longer retention times) were also formed. These compounds were not investigated, but it seems safe to assume that they correspond to the high-boiling products formed from **1**[4a] and thus represent insertion into ether and (formal) dimerization of the $C_{11}H_{18}$ carbenoid intermediates.

The determination of whether or not *cis*- and *trans*-**7** led to different product spectra was made difficult because the partial separation of the isomeric dibromides achieved on analytical glc columns was diminished on preparative scale columns. However, employing glc and microreaction techniques appropriate to the problem, we established that the isomers of **7** did behave differently. The minor (trans) dibromide gave compounds **8**, **10**, and **13** while the major (cis) isomer gave compounds **9**, **11**, and **12**. In each case the reactions are at least 98% stereospecific.

The assignment of stereochemistry to the isomers of **7** is established by these results. Compound **10** can be formed only from the trans dibromide and compound **11** must come from the cis isomer.

The influence of the reaction temperature and the source of the methyllithium used in the reaction on the relative and total yields of the insertion products obtained from the 57:43 mixture of *cis*- and *trans*-**7** was investigated. When methyllithium is prepared from a methyl halide in ether the lithium halide which is formed remains in solution;[21] in our case, the reagent contained either lithium bromide or lithium iodide.[22] In some cases the lithium halide can have a significant effect, either by changing the nature of the carbenoid precursor or by being involved in some other way in the transition states of the subsequent reactions.[23] The results, summarized in Table I, show that the relative yields are nearly independent of the presence or absence of lithium iodide. The most important effect is the large decrease in the total yield at −80°, particularly when lithium iodide is present. In other systems, we have established that the yields of the dimeric products increase when lithium iodide is employed at −80°.[24] Accordingly, glc analysis showed an increase in the formation of high-molecular-weight products believed to be dimers.

Discussion

The stereospecificity in the reaction of *cis*-**7** and *trans*-**7** with methyllithium establishes that a 1,2-cycloheptadiene is not an intermediate en route to the intramolecular insertion products. We can see no reason why the presence of the 3 substituent would have any substantial effect on the ease of opening of the three-membered ring. Hence, we conclude that in general a cyclopropylidene incorporated into a bicyclo[4.1.0]-heptane system does not experience opening and reclosure prior to undergoing C–H insertion. Since the next higher and lower homologs *do open*, the failure of the [4.1.0] system to open may seem anomolous. The fact that the [5.1.0] system does undergo partial ring opening to form 1,2-cyclooctadiene[10] means that, al-

(19) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1882 (1971).

(20) See ref 28. In other systems we have also isolated derivatives of **4** as minor products.

(21) Cooling such solutions causes precipitation of some, but not all, of the lithium halide.

(22) In other studies we have found that employing halide-free methyllithium gives the same results as using methyllithium-containing lithium bromide, presumably because lithium bromide is formed in the reaction: W. R. Moore and C. Kandall, unpublished results.

(23) (a) M. G. Goldstein and W. R. Dolbier, *J. Amer. Chem. Soc.*, **87**, 2293 (1965); (b) G. Closs and C. H. Lin, 20th National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vt., June 1967.

(24) W. R. Moore and M. McGrath, unpublished results.

TABLE I

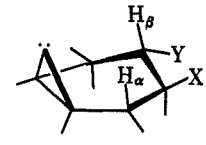
YIELDS OF INTRAMOLECULAR INSERTION PRODUCTS FROM THE 57:43 MIXTURE OF *cis*- AND *trans*-7

Lithium halide	Temp, °C	Percentage of total[a] 8	9	10	11	12	13	Total yield, %
LiBr	0	0.6	0.8	27.9	2.3	49.7	18.7	62
LiI	0	0.5	0.5	28.6	1.9	49.9	18.6	66
LiBr	−80	0.4	0.6	24.7	1.3	52.9	20.1	38
LiI	−80	0.1	0.4	29.6	1.4	51.5	17.0	28
Uncertainty[b]		±0.1	±0.1	±0.6	±0.2	±0.6	±0.4	±2

[a] Each entry represents the mean of the four values obtained from duplicate runs, each run being analyzed twice by glc. [b] The uncertainty represents the 95% confidence interval calculated on the basis of $N = 4$ employing standard deviations determined from the pooled results.

though this allene is certainly strained,[25] and the opening is clearly slowed, the strain is not sufficently high, or at least the extent to which this developing strain is felt at the transition state is not sufficient, to preclude opening in the same sense that is found for most other cyclopropylidenes. The [3.1.0] system leads to 1,2-cyclohexadiene, a planar allene, but the reaction may not involve opening of a cyclopropylidene;[11] rather the α-bromocyclopropyllithium intermediate may rearrange in a manner which is analogous to the carbonium ion rearrangements found for endo-6-substituted derivatives of bicyclo[3.1.0]hexane, rearrangements which are facile because of relief of strain.[26] The bicyclo[4.1.0]-heptane system must lie in a structural region for which opening in the conventional sense to an orthogonal allene is denied because the allene would be too highly strained and yet opening to a planar allene is not favored, primarily because the [4.1.0] system lacks the added strain present in the [3.1.0] system.

In addition to establishing that a 1,2-cycloheptadiene is not an intermediate,[27] the results also provide information concerning the process of intramolecular insertion. The cyclopropylidene intermediates must have half-chair conformations with the *tert*-butyl groups equatorial and thus can be represented as **14** and **15** (shown as "free carbenes" for simplicity). In these conformations, insertion can only occur into the axial C–H bonds indicated as H_α and H_β; as models will show, all equatorial positions are clearly much too far from the carbenoid center to permit insertion. Hence **14** would be expected to give only **11** and **12**, while **15** would be expected to give only **10** and **13**.[28] The fact that this selectivity is *observed experimentally* establishes that these half-chair conformations must correctly describe the systems.



14(cis), X = *tert*-Bu; Y = H
15(trans), X = H; Y = *tert*-Bu

Given that intramolecular insertion occurs from conformations **14** and **15**, it is clear that the H_α/H_β selectivity, equivalent to bicyclobutane *vs.* bicyclopentane formation, is drastically different for the two systems. At 0° (lithium bromide) the *cis*-cyclopropylidene **14** gives a ratio of 22 to 1 for bicyclobutane **12** to bicyclopentane **11**, approximately the same as the ratio of bicyclobutane **2** to bicyclopentane **3** obtained when the unsubstituted dibromide **1** was treated with methyllithium.[8,9] On the other hand, the *trans*-cyclopropylidene **15** gives a ratio of 1 to 1.5 for bicyclobutane **13** to bicyclopentane **10**. Clearly in the cis system, the *tert*-butyl group does not affect the relative reactivities of H_α and H_β, indicating that it does not cause appreciable distortion of the conformation compared to that of the unsubstituted compound. On this basis, it would appear that the 33-fold enhancement of the reactivity of H_β relative to H_α in the trans system does not, at least for the most part, result from distorting the normal half-chair conformation in a way which would move H_β toward and H_α away from the carbenoid center. These motions would result if the *tert*-butyl group of **15** were to rock up toward the carbenoid center. However, it is not apparent why such twisting should occur in **15** but not in **14**. Thus the enhanced selectivity of insertion into the C–H_β bond of **15** must result primarily from the electronic effect of the *tert*-butyl group.[29] The C–H_β bond of **15** is tertiary, whereas all other C–H bonds involved in insertion in **14** and **15** are secondary and in general one anticipates a reactivity order for C–H bonds of tertiary > secondary > pri-

(25) 1,2-Cyclooctadiene must have a "conventional" structure; *i.e.*, it must have an orthogonal allenic linkage which is probably slightly twisted.

(26) (a) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962); (b) U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Lett.*, 3639 (1967); (c) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **7**, 588 (1968).

(27) The results also exclude organometallic species, such as 2-lithio-3-bromocycloheptene or a lithium bromide complex of 1,2-cycloheptadiene, having the same carbon skeleton symmetry as the allene from being intermediates.

(28) The formation of bicyclo[3.2.0]hept-6-ene derivatives is also selective; *cis*-**7** gives **9** and *trans*-**7** gives **8**. This selectivity allows assignment of the position of the *tert*-butyl group in **8** and **9** as follows. Bicyclo[3.2.0]-hept-6-ene (**4**) can be regarded as a "valence" isomer of tricyclo[4.1.0.$0^{2,7}$]-heptane (**2**). It appears to be derived from insertion commencing in the same sense as that leading to **2** (*i.e.*, the shift of the H atom occurs from C-2 to C-7) followed at some point by carbon–carbon bond shifts resulting in rearrangement to **4**. Irrespective of the timing of these shifts the C-1,5 bond of **4** must join what would be the C-2 and C-6 positions of **1**. Applying these considerations to the present substituted case, it becomes clear that the "valence" isomer pairs must be **8**, **13** and **9**, **12**. Thus **8** is 3- and **9** is 2-*tert*-butylbicyclo[3.2.0]hept-6-ene. At this time it appears that **8** and **9** may be mixtures of the exo and endo isomers, but we cannot state with certainty that they are or are not. Since this point is of great importance in establishing the mechanism of formation of the [3.2.0] system, it is under investigation.

(29) From the data obtained from the mixture of 57% *cis*- and 43% *trans*-**7**, the yield of intramolecular insertion products is found to be about 57% from *cis*-**7** compared to 68% from trans-**7** (0°, LiBr). In each case the balance of the material appears as higher molecular weight products which result from intermolecular reactions. The latter reactions provide an internal standard of sorts since their rates should be independent of the stereochemistry of the *tert*-butyl group, which is sensibly remote from the carbenoid center. Thus the enhanced reactivity of C–Hβ of **15** is reflected in a net increase in intramolecular insertion products. The fact that the yield of **8** + **13** is 28% based on *trans*-**7** while the yield of **9** + **12** is 55% based on *cis*-**7** does *not* mean that the C–H_α bond of the trans isomer is deactivated, but simply reflects the fact that the competitive insertion into the C–H bond of **15** is more efficient at removing a common intermediate.

mary.[30] This order stems from the ability of an alkyl group to supply electrons to the adjacent electron-deficient center in the transition state of the insertion reaction. Since the effect is large in this case, it indicates that these cyclopropylidenes are highly selective.

Experimental Section[31]

4-*tert*-Butylcyclohexene.—Treatment of 4-*tert*-butylcyclohexanol (Aldrich Chemical Co.) with acetic acid and acetic anhydride gave 4-*tert*-butylcyclohexyl acetate in 96% yield, bp 75–78° (1 mm).

The acetate was pyrolyzed by passing it through a glass helices packed column heated to 570°. Following the usual work-up, distillation afforded an 81% yield of 4-*tert*-butylcyclohexene, bp 66° (20 mm), n^{17}D 1.4606 [lit.[32] bp 65–66° (20 mm), n^{20}D 1.4583]. Glc analysis showed only one peak on Versamide 900, Carbowax 20M, and SE-30. The infrared spectrum showed no bands at 1035 or 996 cm^{-1} (bands reported to be in 1- and 3-*tert*-butylcyclohexene respectively); ^{33}nmr δ 0.83 (s, 9 H), 1.25 (broad m, 3 H), 1.6–2.3 (4 H), 5.68 (broad s, 2 H).

3-*tert*-Butyl-7,7-dibromobicyclo[4.1.0]heptane (7).—A pentane solution of 4-*tert*-butylcyclohexene was slurried with potassium *tert*-butoxide and freshly distilled bromoform was added dropwise while cooling to 0°. After the usual work-up, distillation gave a 63% yield of **7**: bp 96° (0.35 mm); n^{26}D 1.5298; ir (CCl_4) 3000, 2960, 2860, 1476, 1440, 1400, 1370, 1240, 1050 cm^{-1}; nmr δ 0.80 (s, 3.9 H), 0.84 (s, 5.1 H), 0.9–2.2 (complex, 9 H). *Anal.* Calcd for $C_{11}H_{18}Br_2$: C, 42.61; H, 5.85; Br, 51.54. Found: C, 42.74; H, 5.77; Br, 51.52.

Of all the glc columns shown in footnote 31 (except the last three which were not tried), only LAC 2-R-446, LAC-1-R-296 SAIB, Hyprose, UCON polar, and CPS showed partial separation of the two isomers. A 350 × 0.4 cm 10% Craig polyester succinate column at 140° (showing 3600 theoretical plates) gave the best partial separation; the retention time ratio was cis/trans = 1.04. Employing analysis of the peak shapes, the peaks were resolved graphically to enable a determination of the cis:trans ratio, found to be 57:43. This ratio is confirmed by the nmr spectrum in which the same ratio was seen for the *tert*-butyl peaks.

Unfortunately, preparative separation by glc was made very difficult because the peaks broadened and merged when the sample size was increased (analytical measurements employed a flame ionization detector and very small samples). By repeated collection of the front and back of the merged peak, it was possible to obtain samples of the order of 1 mg which were enriched in the trans and cis isomers but were not pure. In order to obtain each isomer as pure as possible, small glc samples were employed and only *ca.* 1% of the extreme front and rear of the merged peak was collected, affording quantities of the individual isomers estimated to be *ca.* 0.01 mg.

3-*tert*-Butylbicyclo[4.1.0]heptane.—Reduction of **7** with sodium in liquid ammonia followed by work-up and distillation gave 3-*tert*-butylbicyclo[4.1.0]heptane: bp 72° (21 mm); nmr δ −0.1 (m, 1 H), 0.2–2.4 (broad and complex, 19 H, but with two *tert*-butyl singlets totaling 9 H at 0.78 and 0.80 having a ratio similar to that for **7**); mass spectrum *m/e* 152 (M$^+$). Although this material was definitely a mixture of isomers based on the nmr spectrum, it gave a single peak on several glc columns. *Anal.* Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.88; H, 13.04.

Reaction of 7 with Methyllithium.—Methyllithium (0.020 mol) in ether was added to a solution of 5.0 g (0.016 mol) of **7** in 20 ml of ether maintained at 0°. Water was added and the ether layer was separated and dried (Na_2SO_4). The volatile materials were distilled at 25° (0.05 mm) into a trap maintained at −78°. The distillate was concentrated by distillation using a 26 × 1 cm Vigreux column. Glc analysis (350 × 0.2 cm, 2% Carbowax 20M on basic Chromosorb P, 98°) showed the six-component mixture with the following retention times relative to *p*-xylene (1.00): **8** (1.30), **9** (1.40), **10** (1.63), **11** (1.74), **12** (2.17), **13** (2.54). The compounds were collected from preparative glc columns; spectral and analytical data are presented later. In order to prevent rearrangment of the bicyclobutanes which are very sensitive to acids, it was absolutely imperative to wash all glassware with alkaline methanol, to use base-washed glc supports, and to use either on-column injection or clean inserts in the inlet system of the glc instruments.

The nonvolatile residue from the distillation was analyzed by glc (SE-30, 90 → 240°) showing that it was a complex mixture of products with retention times similar to that of the starting dibromide. This material was not investigated further.

The reaction was repeated employing 1 mmol of **7** in 6 ml of ether. Methyllithium prepared from both methyl bromide and methyl iodide was used and reaction temperatures were maintained at 0 and −80°. The reaction mixture was analyzed directly after hydrolysis (without distillation) employing *p*-xylene as an internal standard. In each case duplicate runs were made and each reaction mixture was analyzed twice. The averages of these determinations are given in Table I.

In order to carry out the reaction reproducibly on a very small scale, the following technique was employed. A melting point capillary sealed at one end was placed in a 10 × 1.5 cm glass tube also sealed at one end. After both tubes had been dried at 160°, they were flushed with nitrogen and the outer tube was sealed while warm with a "No-Air" stopper. The apparatus was cooled and 0.5 ml of 0.5 *M* methyllithium in ether was injected (syringe) into the outer tube to serve as a drying agent and oxygen scavenger. If the solution did not turn cloudy, *ca.* 2 μl of **7** was injected (microliter syringe) into the inner tube. The apparatus was cooled to 0° and 50 μl of 0.5 *M* methyllithium solution was injected (microliter syringe) into the inner tube. The reaction mixture was allowed to warm to room temperature and then was analyzed directly by glc (Carbowax 20M). On-column injection was employed utilizing a replaceable section at the front of the column (which served to hydrolyze excess methyllithium). Using the 53:47 mixture of *cis*- and *trans*-**7** and methyllithium prepared from methyl bromide, this procedure was found to give results (the average of nine reactions) which were indistinguishable from those in Table I. Employing several 0.5–1-mg samples of **7** collected by glc and enriched in either isomer led to enrichment in the $C_{11}H_{18}$ products in the sense indicated previously. With the very small samples of **7** (*ca.* 0.01 mg, transferred from the glc collectors with a few microliters of ether), 10 μl of methyllithium was used and the entire reaction mixture was injected in one pass in the glc analysis. These reactions established a lower limit of 98% in the stereospecificity based on the estimated detection limits.

2- and 3-*tert*-Butylbicyclo[3.2.0]hept-6-ene (8 and 9).—The mixture (*ca.* 1:1) was collected by glc employing an XE-60 column: ir (CCl_4) 3025, 2950, 2860, 1720, 1470, 1390, 1365 cm^{-1}; nmr (CCl_4) δ 0.81, 0.89, 0.94 (three s, ~9 H, *tert*-butyl) superimposed on 0.8–2.3 complex multiplet (~5 H), 3.2 (d, 2 H), 5.85 (s, 2 H); mass spectrum *m/e* (rel intensity) 150 (M$^+$, 0.5), 135 (4), 107 (7), 94 (15), 93 (27), 91 (14), 80 (27), 79 (28), 77 (15), 57 (100), 55 (11), 41 (38), 39 (23).

5-*tert*-Butyltricyclo[3.2.0.0^{2,7}]heptane (10).—The compound was collected by glc employing a Carbowax 20M column: ir (neat) 3050, 3030, 2955, 2900, 2865, 1475, 1395, 1365, 1325, 1220, 1245, 1180, 1118, 962, 915, 895, 840, 810, 800, 770, 725, 690 cm^{-1}; nmr (CCl_4) δ 0.94 (s, 9 H), 1.06 (d, 1 H), 1.2–1.45 (m, 3 H), 1.45–1.8 (m, 1 H), 1.8–2.3 (m, 4 H); mass spectrum *m/e* (rel intensity) 150 (M$^+$, 3), 135 (58), 122 (3), 107 (37), 94

(30) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 55.

(31) Infrared spectra were determined with Perkin-Elmer Models 237 and 337 spectrophotometers. Nmr spectra were obtained on a Varian A-60 spectrometer. Mass spectra were determined on a Consolidated Electrodynamics Model 21-130 mass spectrometer with an ionizing potential of 68 V (inlet system heated to 135°). The gas chromatography apparatus utilized thermal conductivity detectors (homemade, all glass) or flame ionization detectors with (F & M Model 810) or without (Wilkins Model A-600) a carrier gas stream splitter. Columns were 300–350 × 0.2 cm for analytical (2–10% liquid phase) and 200–350 × 1.0–1.4 cm (10–20% liquid phase) for preparative purposes. Liquid phases employed (on neutral or basic Chromosorb P) were Carbowax 20M, silicone nitrile (XF-1150), silicone nitrile (XE-60), Craig polyester succinate (CPS), SE-30 silicone rubber, ethylene glycol adipate, Versamide 900, silicone 200, LAC-2-R446, LAC-1-R296, Tide (40–60 mesh), sucrose acetate isobutyrate (SAIB), Hyprose, "air-blown" asphalt, *m*-bis(diphenoxy)benzene, tricresylphosphate, UCON Polar, tricyanoethoxypropane (TCEP), tetraethylene glycol (TEG), 3-nitro-3-methylpimelonitrile (NMPN), and silver nitrate–ethylene glycol. Gas chromatographic analyses employed internal standards utilizing appropriate response factors with peak areas determined by planimetering. Elemental analyses were performed by Dr. S. M. Nagy and associates at the Massachusetts Institute of Technology. All melting points and boiling points are uncorrected. All reactions employing organometallic reagents, active metals, alkoxides, or hydrides were conducted under a nitrogen atmosphere.

(32) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5577 (1955).

(33) H. L. Goering, R. L. Reeves, and H. H. Espy, *ibid.*, **78**, 4926 (1956).

(37), 93 (100), 92 (13), 91 (32), 83 (12), 81 (12), 79 (37), 77 (27), 67 (10), 65 (10), 57 (63), 55 (28), 53 (13), 43 (16), 41 (58), 39 (38). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.10; H, 12.03.

exo-4-*tert*-**Butyltricyclo[3.2.0.0^{2,7}]heptane** (**11**).—The compound was collected by glc employing an XF-1150 column: ir (CCl_4) 3055, 3030, 2960, 2900, 2856, 1470, 1395, 1365, 1300, 1245, 1210, 1075, 955, 890 cm^{-1}; nmr (CCl_4) δ 0.80 (s, 9 H), 0.8–1.7 (m, 4 H), 1.7–2.15 (m, 4 H), 2.15–2.6 (m, 1 H); mass spectrum *m/e* (rel intensity) 150 (M^+, 1) 135 (2), 107 (5), 93 (6), 91 (7), 79 (9), 77 (7), 69 (9), 67 (8), 66 (100), 57 (33), 41 (20), 39 (11).

3-*tert*-**Butyltricyclo[4.1.0.0^{2,7}]heptane** (**12**).—The compound was collected by glc employing a Carbowax 20M column: ir (CCl_4) 3083, 2990, 2960, 2860, 1475, 1393, 1365, 1238, 1225, 1130, 975 cm^{-1}; nmr (CCl_4) δ 0.88 (s, 9 H, *tert*-butyl), 1.51 (t, 2 H, C-1,7) superimposed on 0.9–1.6 (broad m, 5 H), 2.36 (m, 2 H, C-2,6); mass spectrum *m/e* (rel intensity) 150 (M^+, 5) 135 (4) 107 (2), 94 (48), 93 (14), 91 (12), 79 (29), 77 (13), 57 (100), 41 (31), 39 (16). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.08; H, 12.06.

4-*tert*-**Butyltricyclo[4.1.0.0^{2,7}]heptane** (**13**).—The compound was collected by glc employing a Carbowax 20M column: ir 3090, 2995, 2960, 2860, 1475, 1390, 1365, 1290 (d), 1240, 1175, 1135, 1060, 980 cm^{-1}; nmr (CCl_4) δ 0.78 (s, 9 H, *tert*-butyl), 1.46 (t, 2 H, C-1,7) superimposed in 0.8–1.3 (broad m, 5 H), 2.34 (m, 2 H, C-2,6); mass spectrum *m/e* (rel intensity) 150 (M^+, 12), 135 (4), 107 (9), 94 (25), 93 (18), 91 (14), 79 (28), 77 (12), 57 (100), 41 (20), 39 (15). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.09; H, 12.09.

The nmr spectra of **12** and **13** did not change significantly when taken in chloroform, benzene, pyridine, or methanol.

3-Methyl-7,7-dibromobicyclo[4.1.0]heptane.—Commercial 4-methylcyclohexene (Eastman Kodak White Label) was found to contain 11% of isomeric impurities, mainly 3-methylcyclohexene, as shown by glc analysis on an ethylene glycol–silver nitrate column. Hence 4-methylcyclohexyl acetate was prepared and pyrolyzed[34] at 570° to give 4-methylcyclohexene in 80% yield, n^{24}D 1.4389 (lit.[34] n^{20}D 1.4414), which was shown by glc to be free of isomers.

Dropwise addition of 253 g (1 mol) of bromoform to a cold slurry (both at −15°) of 1 mol of potassium *tert*-butoxide, 29 g (0.96 mol) of 4-methylcyclohexene, and 500 ml of pentane followed by the usual work-up gave 144 g (54%) of 3-methyl-7,7-dibromobicyclo[4.1.0]heptane: bp 62–64° (0.25 mm); n^{26}D 1.5419; ir 2970, 2900, 2820, 1445, 1380, 1335, 1460 cm^{-1}. *Anal.* Calcd for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.63. Found: C, 36.02; H, 4.59; Br, 59.68.

All attempts to crystallize this dibromide at low temperatures failed. Glc in all columns listed in footnote 31 except the last three (not tried) showed only one peak.

Reduction of the dibromide with sodium in liquid ammonia employing ether as a cosolvent followed by the usual work-up gave 3-methylbicyclo[4.1.0]heptane, collected by glc (silicone 200, to remove a 6% impurity), mass spectrum *m/e* 110 (M^+). Analysis of this material in a 60-m polyethylene glycol capillary glc column[35] showed two peaks with very close retention times in an area ratio of 43:57.

Addition of the Simmons–Smith reagent[36] to 4-methylcyclohexene gave 3-methylbicyclo[4.1.0]heptane having a mass spectrum identical with that of the sample obtained from reduction of the dibromide. Capillary column glc analysis showed the same two peaks in an area ratio of 44:56.

Registry No.—*cis*-**7**, 29339-16-0; *trans*-**7**, 29339-17-1; **8**, 29339-18-2; **9**, 29339-19-3; **10**, 29339-20-6; **11**, 29339-21-7; **12**, 29488-51-5; **13**, 29339-23-9; methyllithium, 917-54-4; 3-methyl-7,7-dibromobicyclo[4.1.0]heptane, 29339-24-0; *cis*-3-*tert*-butylbicyclo[4.1.0]heptane, 29339-25-1; *trans*-3-*tert*-butylbicyclo[4.1.0]heptane, 29339-26-2.

(34) E. Gil-Av, J. Herling, and J. Shabtai, *J. Chromatogr.*, **1**, 508 (1958).

(35) We are indebted to Dr. E. P. Blanchard, Jr., of the E. I. du Pont de Nemours and Co., Inc., for the capillary column analyses.

(36) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

Derivatives of Bicyclobutane and Bicyclo[2.1.0]pentane. Establishment of the Structures of 3- and 4-*tert*-Butyltricyclo[4.1.0.0^{2,7}]heptane and 5- and *exo*-4-*tert*-Butyltricyclo[3.2.0.0^{2,7}]heptane[1]

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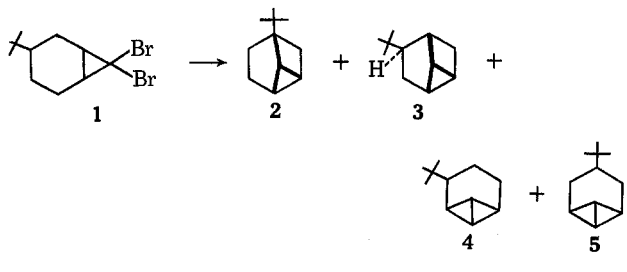
The structures of bicyclo[2.1.0]pentane derivatives **2** and **3** have been established by hydrogenation to **8** and **15**, respectively, compounds which were synthesized independently. Treatment of **2** with aluminum chloride resulted in rearrangment to an isomer assigned structure **11**. Bicyclobutane derivative **4** was isomerized by magnesium bromide in ether to **17**, **18**, and **19**, while **5** gave **20** and **21**. These results distinguish between **4** and **5** and, when product ratios are considered, provide a basis for suggesting how the rearrangements occur.

The treatment of a mixture of 57% *cis*- and 43% *trans*-3-*tert*-butyl-7,7-dibromobicyclo[4.1.0]heptane (**1**) with methyllithium produced four tricyclic hydrocarbons **2**, **3**, **4**, and **5**.[3] While the spectral properties of these products were sufficient to define **2** and **3** as *tert*-butyl derivatives of tricyclo[3.2.0.0^{2,7}]heptane (**6**) and **4** and **5** as *tert*-butyl derivatives of tricyclo[4.1.0.0^{2,7}]heptane (**7**), the position of the *tert*-butyl group



in each case was assigned solely on the basis of mass spectral data. Since our arguments really set, rather than rely on precedent, we undertook to define the structures chemically by unequivocal means and hoped that in the process we would establish some reaction patterns for these and related systems.

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(2) National Institutes of Health Predoctoral Fellow, 1962–1965.

(3) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1877 (1971).