The Consequences of Methyl Substitution on the Efficiency and Regioselectivity of C–H Insertion during Intramolecular Cyclization of Norcaran-7-, 3-Norcaren-7-, and Tricyclo[5.1.0.0^{3,5}]octan-8-ylidenes

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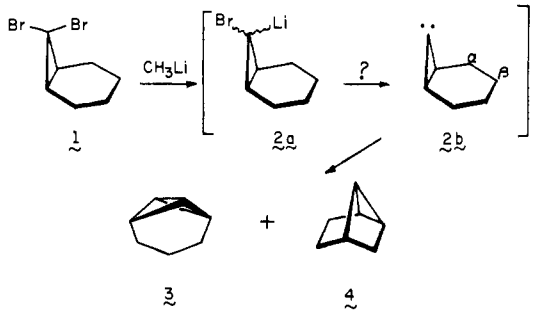
Abstract: The reaction of ethereal methyllithium with a variety of methyl-substituted 7,7-dibromonorcaranes has been investigated. The carbenoids so generated enter into intramolecular C–H insertion to give tricyclo[4.1.0.0^{2,7}]heptanes, tricyclo[4.1.0.0^{3,7}]heptanes, and/or tricyclo[3.2.1.0^{2,7}]octanes, whose structures have been elucidated by chemical and spectral means. The results require that methyl groups which are axially disposed and syn oriented to the carbenoid center dominate the cyclization by providing sufficient steric congestion to facilitate closure. When the alkyl groups are equatorial, insertion into the vicinal C–H bond is markedly improved. It is proposed that this reactivity pattern reflects the positive inductive effect of $-CH_3$ on neighboring bond nucleophilicity. When at least one methyl resides at a ring juncture, resulting nonbonded steric interactions cause conformational twisting which fosters greater proximity to the axial C_2–H_α bond and high levels of reactivity at this site. These steric results were then employed to advantage in the preparation of the heretofore elusive tricyclo[4.1.0.0^{2,7}]-hept-3-ene and tetracyclo[5.1.0.0^{2,4}.0^{3,5}]octane ring systems. For comparison purposes, 7-norcaranylidenes geminally substituted with methyl groups at C_4 were also examined. In these reactive intermediates, steric and ponderal effects gain importance and retard the rate of interconversion between the two low-energy conformations such that ring flipping becomes competitive with the various possible C–H insertions.

From among the numerous synthetic approaches to the bicyclo[1.1.0]butane ring system currently available, that discovered in 1961 by Moore[2] has played a most important role. Additionally, the stereospecific intramolecular cyclizations of **2** into both C–H_α and C–H_β are processes central to

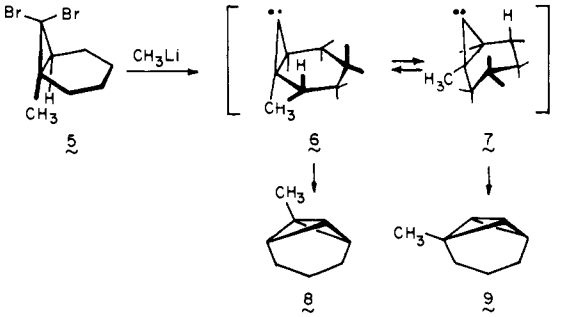


our understanding of the mechanisms by which such carbenoids[3] undergo insertion into neighboring carbon–hydrogen bonds. It is clear, especially from more recent investigations,[4-8] that these stereospecific reactions proceed only from those conformations in which the particular C–H bond under siege is oriented axially (retention of configuration necessarily results) and that triangular transition states[9] rather than theoretically favored linear approaches[10] are involved. Because of the prevailing geometric restrictions, the indicated intramolecular captures of 7-norcaranylidenes (e.g., **2**) appear to be highly sensitive to conformational and substituent effects, at least those resulting from methoxyl groups.[7,8] For example, it is now clear that (1) an equatorial α-OCH_3 group deactivates insertion into the adjoining axial C–H_α bond; (2) an equatorial β-OCH_3 substituent reverses the trend and actually promotes cyclization at C–H_β; and (3) an axial α-OCH_3 causes ready carbenoid insertion into the antiplanar C–H_β bond. These observations have been interpreted on the basis of an early transition state for C–H_α abstraction with bond nucleophilicities being dominant and a later transition state for C–H_β attack with the result that electronic factors have greater impact.[8]

This paper describes an investigation aimed at revealing more clearly the effect of various methyl substitution plans on the reactivity patterns of 7-norcaranylidenes. Having shed light on this problem, we proceed to apply these findings to the preparation of the formerly elusive tricyclo[4.1.0.0^{2,7}]hept-3-ene and tetracyclo[5.1.0.0^{2,4}.0^{3,5}]octane classes of hydrocarbons.[11] Neither of these highly strained molecular frameworks has previously commanded widespread attention because of their presumed inaccessibility. In addition to broadening the base of synthetic small ring chemistry, the results reported here further clarify several additional factors which are of importance to intramolecular carbenic processes.

Results

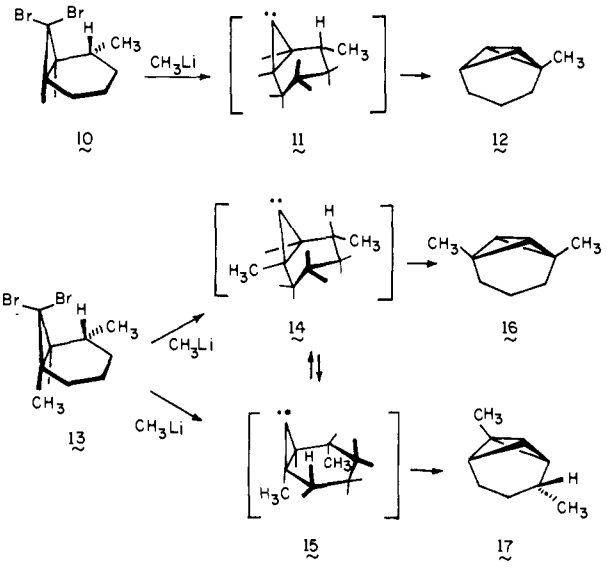
Reactions of 7-Norcaranylidenes. Whereas the reaction of **1** with methyllithium in ether yields **3** and **4** in a 23:1 ratio,[2] Reinarz and Fonken have observed that the presence of a 1-methyl substituent as in **5** serves to deter C–H_β insertion al-



together and to promote higher conversion to tricycloheptane products.[6] Not only is intramolecular attack on the "exterior" methyl group not observed (the 1-isopropyl and 1-*tert*-butyl derivatives behave comparably[7,12]), but the 60:40 distribution of **8** and **9** denotes a slight preference for closure from half-chair conformation **6** rather than **7** (the C–H bonds involved in further reaction of each carbenoid will herein be denoted specifically by an H symbol). Addition of a second angular methyl group at C_6 is known also to facilitate carbenoid cy-

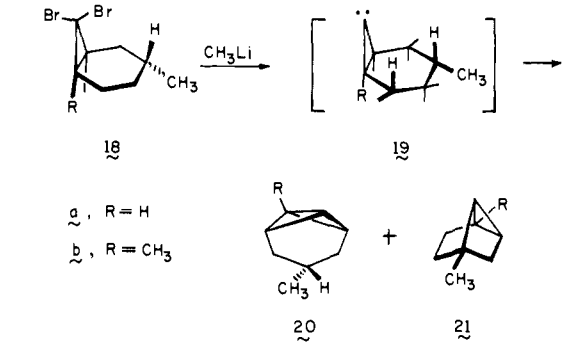
clization into the proximal C–H_α bonds (now equivalent),[5] at least when the cyclohexyl ring is otherwise unsubstituted.

Presently, there can be little doubt that a 1-methyl group acts in a subtle way on the 7-norcaranylidene framework to promote enhanced levels of syn-H_2 abstraction as well. This is obvious simply by inspecting the behavior of the *anti*-5-methyl (**10**,[5] **13**[7]) and *anti*-4-methyl dibromonorcarane pairs



(**18a**,[8] **18b**). Thus exposure of **10** (admixed with **30a** from which it cannot be readily separated) to ethereal methyllithium at 0 °C results in the exclusive formation of tricycloheptane **12.** Not only is C–H_β insertion again not in evidence, but the observed regiospecificity requires that tricycloheptane **12** arise by carbenoid attack on that axial H_α present in conformer **11.** The indication is therefore that the 5-methyl group in **10** significantly enhances the level of reactivity at C_5. Despite this, placement of a second methyl group at C_1 as in **13** successfully shunts 10% of the total reaction profile away from **14** and toward **15** to give a hydrocarbon mixture consisting of both **16** and **17** (9:1). Accordingly, we see that less stable conformer **15** now finds it possible to compete in the product-forming manifold. But how is it that **15** enjoys sufficient reactivity advantage to vie with **14** (note that C_2–H_α lacks the supportive electronic contributions of a methyl appendage and is therefore not an activated site)?

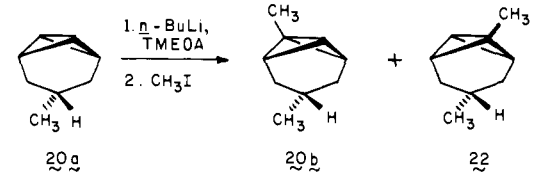
Before responding to this question, let us first analyze the product distributions given by **18a** and **18b.** It has previously



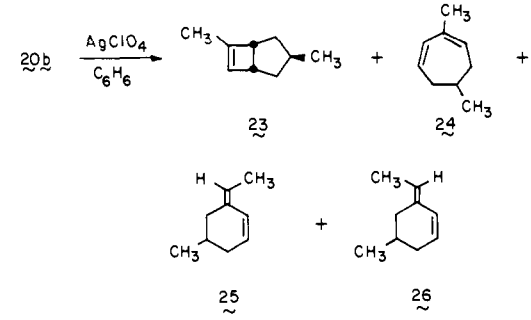
been shown that treatment of the first of these dibromides with methyllithium in the usual manner affords **20a** and **21a** in a ratio of 2.3:1.[8] Both of these products can be accounted for in terms of the more stable carbenoid conformation **19a.** The H_α/H_β reactivity profile of 2.3, which denotes a tenfold greater capability for H_β insertion relative to parent carbenoid **2**,[13] again emphasizes the directing capabilities of a β-alkyl group in such reactions.

When dibromocarbene was added to 1,4-dimethylcyclohexene, there was obtained an inseparable mixture of **18b** and **33b** in a ratio of 60:40. Combined reaction with methyllithium afforded in 76% yield a mixture consisting of **20b** (50%), **21b** (6%), **36b** (16%), and **37b** (28%). These products were successfully separated by preparative VPC techniques and individually characterized by ^{1}H NMR spectroscopy. The very characteristic signals of **21b** include a pair of methyl singlets at δ 1.12 and 1.08 (thereby denoting attachment to tetrasubstituted carbon) and a remaining multiplicity and chemical shift pattern very similar to that of the monomethyl derivative.[8] The isolation of **21b** establishes the capability of conformation **19b** for insertion into that C–H_β bond vicinal to the remote methyl substituent.

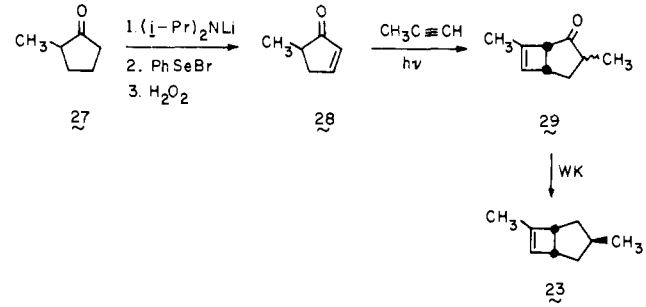
Although tricycloheptane **20b** exhibits in its high-field NMR region several complex patterns which parallel closely those of related molecules, the spectrum did not provide convincing evidence either for the specific location of the secondary methyl group or its stereochemical disposition relative to the bridgehead methyl. Independent evidence for the 1,4-disubstitution plan was first obtained by metalative alkylation of **20a.** There resulted two isomeric hydrocarbons, one of which



was identical with the cyclization product isolated earlier. An unequivocal distinction between **20b** and **22** was subsequently undertaken on the basis of the known ability of 1-methyl substituents to direct Ag^+-catalyzed tricycloheptane rearrangements chiefly into the type γ isomerization channel.[8,14] In the present instance, exposure of the dimethyltricycloheptane to a catalytic amount of $AgClO_4$ in benzene led to the formation of **23** (51%), **24** (28%), **25** (13%), and **26** (8%). In-



dependent synthesis of bicycloheptene **23** was in turn achieved by [2 + 2] photocycloaddition[8,15,16] of propyne to 5-methyl-2-cyclopentenone (**28**) and Wolff–Kishner reduction of adduct



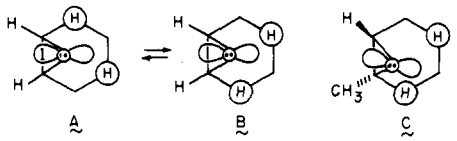
29 under conditions where full thermodynamic equilibration could be attained. The hydrocarbon so produced was identical with **23.** Since the type γ isomerization of tricycloheptanes is completely stereospecific,[8] **23** can only arise from **20b** which

must itself arise from carbenoid insertion into the C_2–H_α bond of **19**.

Authentic samples of **25** and **26** were prepared by treatment of 5-methyl-2-cyclohexenone under classical Wittig conditions with ethylidenetriphenylphosphorane.

Since **36b** and **37b** arise from **33b** (see below), the distribution between **20b** and **21b** (8.3:1) provides a direct measure of the increased degree of C_2–H_α insertion which accompanies a change in R from H to CH_3 in **19**.

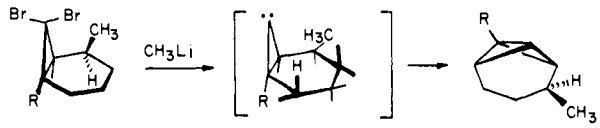
As judged from molecular models those steric factors which come into play upon introduction of a methyl group at C_1 of the 7-norcaranylidene frame consist of nonbonded interactions with H_2 and H_6. The emergence of such eclipsing strain in both available low-energy conformations (top views given by A and B) seemingly promotes twisting about the cyclopropane ring



A B C

so as to project the C_1 substituent in a pseudoaxial direction.[17] The resultant canting of the carbenic p orbital introduces a proximity to C_2–H_α (cf. C), the magnitude of which is less than any of the C–H_α distances prevailing in A and B. Such a perturbation of the carbenoid center simultaneously increases the distance from C_7 to the C_4–H_β bond. To the extent that such unstable energetic intermediates engage in chemical reaction according to their relative proximity to axially oriented nucleophilic C–H bonds (rather than on the basis of product stability, for example), then the causative factors underlying the enhanced levels of C_2–H_α reactivity and the absence of C_4–H_β insertion within **11/14,15** and **19a/19b** finds explanation in the model provided by C.

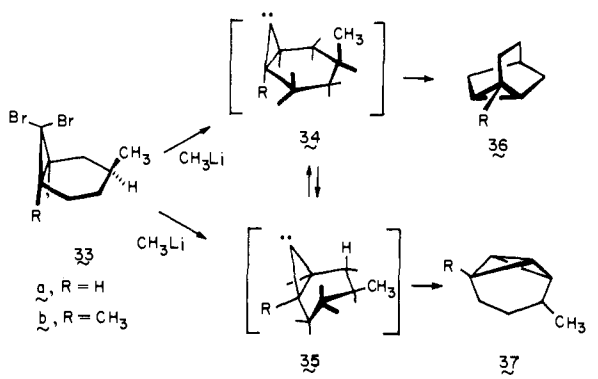
The *syn*-5-methyl derivatives **30a** and **30b** are so constructed that their derived carbenoids react exclusively via the particular conformer which avoids direct cyclopropyl–axial methyl confrontation, namely, **31**.[5,8] As a result of such stereopopulation control, C_2–H_α insertion is fostered in either case and the reactivity impact of the 1-methyl substituent in **30b** is masked.



30 31 32

a, R = H ; b, R = CH_3

Because comparable factors do not gain importance when the methyl substituent is syn oriented at C_4 as in **33a** and **33b**, these examples provide additional clear support for the earlier rationalization. Thus, the efficient conversion of dibromide **33a** to tricyclo[3.2.1.$0^{2,7}$]octane (**36a**)[8] demands a reaction coordinate involving the more strained intermediate **34a** which

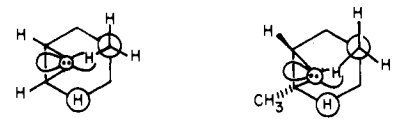


33 34 35 36 37

a, R = H
b, R = CH_3

delivers product exclusively by insertion into the axial methyl group. In the cyclization of **33b**, the additional 1-methyl group does not act as a deterrent to this insertion scheme in a manner which promotes alternative attack at C_2–H_α. The relative yield of **36b** does drop to 36%, with the major portion of carbenoid capture now being drained off to give **37b**. However, accountability for the latter hydrocarbon can be traced to conformation **35b** which now may gain importance relative to **34b** because of the axial nature of both methyl groups in the latter (see structure).

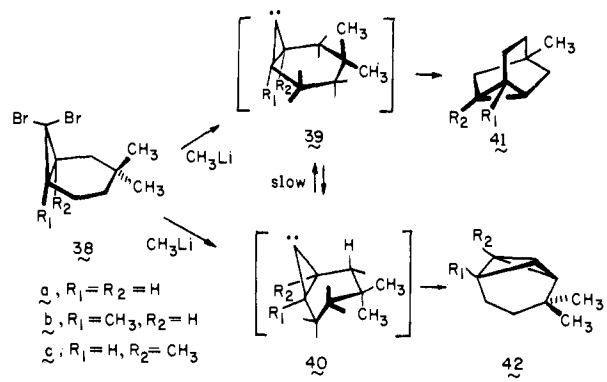
These results show that an axial 4-methyl group precludes detectable attack at the C_2–H_α bond despite its similar axial orientation. Below, intermediates **34a** and **34b** are drawn in the top views D and E, respectively. Insofar as proximity effects



D E

are concerned, molecular models of D reveal the angular methyl hydrogens to be projected on a time-averaged basis directly into the p orbital at C_7, a compression which is not attenuated even when the norcaranylidene framework is somewhat twisted as in E. Again it is possible to account for the observed product distributions strictly in terms of an internally consistent set of steric criteria.

When C_4 is geminally disubstituted, still other controlling factors are made clear. Cyclization of dibromide **38a**, the "model" of the series, in first considered. When treated in the predescribed manner, **38a** was transformed into **41a** and **42a**, with the former predominating by a factor of 10:1. The identity of **41a** was recognized spectroscopically by the great similarity



38 39 40 41 42

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$, $R_2 = H$
c, $R_1 = H$, $R_2 = CH_3$

of its ^1H NMR spectrum with that of the parent ring system and on the basis of a single methyl resonance (δ 0.83, s) of area 3. As expected for the unsymmetrical nature of tricycloheptane **42a**, its "wing" protons (H_2 and H_6) are clearly nonequivalent. The large preference for syn methyl insertion is again obvious, although it falls short of being the exclusive reaction channel (compare **33a**).

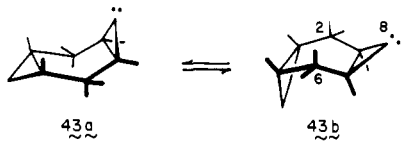
Attention was next turned to **38b**, the product of dibromocarbene addition to 1,4,4-trimethylcyclohexene, which when treated as before with ethereal methyllithium underwent cyclization to give **41b** and **42b**. The relative distribution of these products was 45 and 55%, respectively, corresponding to a significant increase in C_5–H_α reactivity. The correspondence with the reactivity profile of **33b** is particularly striking.

In their recent examination of the intramolecular carbenoid insertion of **38c**, Cory and co-workers have established that a comparable partitioning to give **41c** (40%) and **42c** (60%) is again operative.[18] Once more, unusually high levels of C–H_α insertion at an unactivated site gain importance.

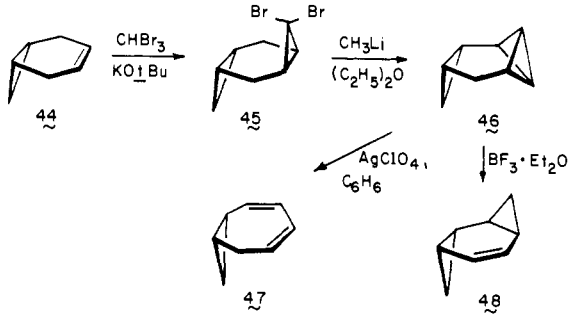
The regiospecificity for syn methyl insertion in **39** accords well with our prior assumption that the most reactive transition

state is also the most sterically encumbered. This analysis does not, however, predict that C_5–H_α insertion via **40** should be a competitive mode of cyclization. It may be argued, however, that internal rotations in this system have now become slow relative to carbenoid capture. This argument cannot apply to **33a** where conformational interconversion between **34a** and **35a** could be slower than attack at methyl but necessarily faster than carbenoid capture by the axial C_5–H_α bond (in **35a**). As concerns the carbenoids derived from **33b** and **38a–c,** however, the additional methyl substituents appear to exert both ponderal[19] and steric effects such that ring flipping now is fully competitive with the various possible C–H insertions. Advocacy of this mechanistic rationale takes its justification from the Curtin–Hammett principle,[19] the key feature of which entails that the transition state separating, for example, **39a** from **40a** be more energetically demanding than those involving conversion of either carbenoid to its cyclized product.

Generation and Cyclization of Tricyclo[5.1.0.0^{3,5}]octan-8-ylidenes. Appendage of an anti-fused cyclopropane ring to C_3–C_4 of 3-norcarene engenders some noteworthy conformational changes relative to the simpler norcaranes. A most important consequence of this substitution plan is to restrict the molecular framework to two low-energy forms, subsequently referred to conveniently as the cis-boat and trans-boat conformers. When the methylene carbon of one three-membered ring is then provided with carbenoid character as in **43,** the aforementioned steric requirement for intramolecular cyclization is met only by that conformation having syn-axial C–H_α bonds, viz., **43b.** It should follow that closure occur exclusively from the trans-boat structure and we therefore sought to determine not only the feasibility of such carbenic insertion but its efficiency as well. The overall impression gained from inspection of molecular models was that C_8 was now held somewhat more remotely from the prospective sites of insertion (C_2–H and C_6–H) than in the intermediates heretofore studied.

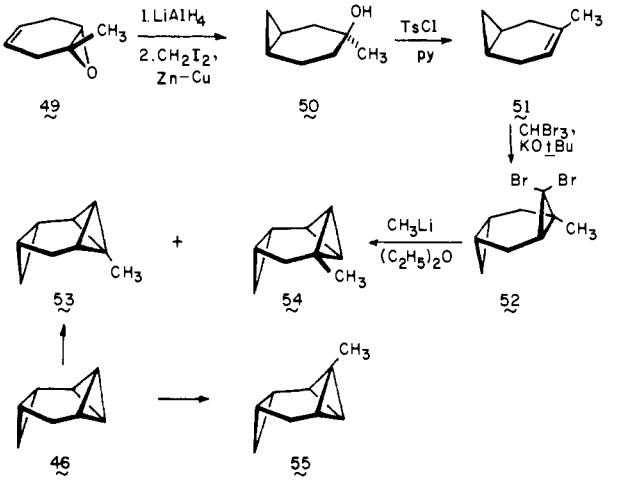


The action of dibromocarbene on **44** gave dibromide **45**, the trans stereochemistry of which was established previously by Winstein and co-workers on the basis of dipole moment measurements.[20] This compound proved highly reactive to ethereal methyllithium at −20 °C, cyclization occurring efficiently to give tetracyclo[5.1.0.0^{2,4}.0^{3,5}]octane (**46**) in 91% yield. This hydrocarbon exhibits (in C_6D_6 solution) a ^{1}H NMR spectrum characterized by multiplets at δ 2.70–2.50 (1 H), 2.20 (1 H), 1.84–1.44 (2 H), 1.32–1.08 (2 H), 0.98–0.64 (1 H), and 0.60–0.16 (3 H). Chemical confirmation of the structural assignment was realized by quantitative isomerization to 2,3-homotropilidene (**47**) in the presence of catalytic amounts of silver perchlorate in anhydrous benzene solution and by Lewis acid promoted ring opening to *trans*-bishomobenzene (40%).

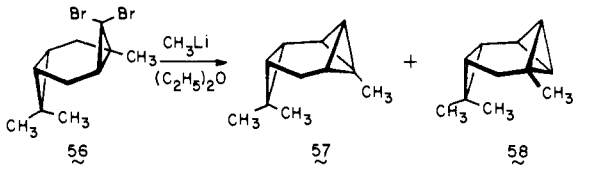


As a route to **47,** the present method is more preparatively useful than that involving the cyclopropanation of tropilidene,[21] since the 4,5 isomer is not produced as a contaminant. Similarly, the elaboration of **48** here described stands as the most ready source of this hydrocarbon yet reported.[22,23]

While carbenoid **43** is obviously capable of efficient intramolecular insertion, its intrinsic symmetry does not permit a distinction to be made between either of the two (herein equivalent) C–H_α bonds during conversion to **46.** Since it had been demonstrated earlier that a 1-methyl substituent promoted enhanced C_2–H_α attack in more flexible 7-norcaranylidenes, we were led to examine its effect upon tricyclo[5.1.0.0^{3,5}]octan-8-ylidene reactivity. Our approach to **52** involved epoxidation of 2,5-dihydrotoluene,[24] followed by lithium aluminum hydride reduction and Simmons–Smith cyclopropanation of **49.** Dehydration of **49** with *p*-toluenesulfonyl chloride in pyridine[25] proceeded with introduction of an endocyclic nonconjugated double bond to give **51** almost entirely. The stereochemical results of dibromocarbene addition provided no surprises. Exposure of **52** to methyllithium as before produced two isomeric tetracyclic products in a ratio of 5:1. The dominant isomer was identified as **53** on the basis of its independent synthesis from **46,** the methylation of which also gave rise to **55.**



The same discrimination was observed upon cyclization of **56** which was readily prepared from 3-carene. In this instance, the more crowded tetracyclooctane **57** was formed preferentially to its positional isomer **58** by a factor of 3:1.

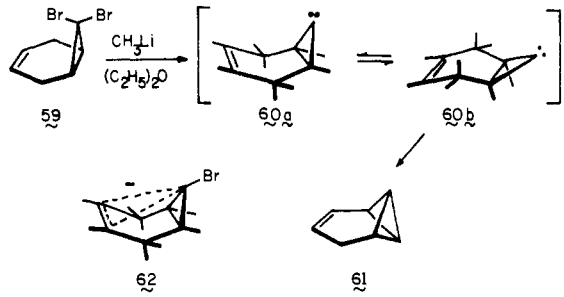


Thus, the available data depict a role for the C_1 angular methyl group comparable to that found in 7-norcaranylidenes. In our view, a ready and cogent explanation for the enhanced insertion into C_2–H_α is again provided by the methyl steric effect which causes conformational distortion to that direction which orients the carbenoid center closer to C_2.

One additional factor deserves mention in this regard. There is no evidence available at present which allows a precise assignment of conformation to tricyclo[5.1.0.0^{3,5}]octane derivatives. In actuality, structures related to **43** could be substantially more shallow than illustrated. 1,4-Cyclohexadiene, for example, is generally considered to be boat shaped,[26] although spectral evidence that it is nearly a flat molecule does exist.[27]

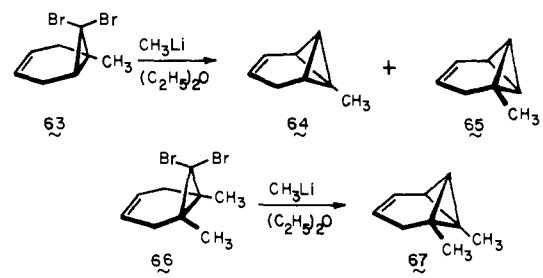
The ^1H NMR spectrum of the homologous 3-norcarane structure is seemingly consistent with either a flat or cis-boat conformation.[28] Although the trans-boat form may be less stable at ambient temperature, this particular conformation is certainly available to partake in chemical reaction.[29] The sensitivity of this conformational equilibrium to substitution of either the cyclopropane or cyclohexane ring has also previously been commented upon.[29] If flatness in these six-membered rings is enhanced by increased internal bond angles and augmented s character in the constituent carbon–carbon bonds, such as would result upon multiple cyclopropanation as in **45, 52,** and **56,** then the lowest energy states of these molecules and their carbenoids could be flattened relative to **43,** If such is the case, then a 1-methyl substituent would experience somewhat greater nonbonded steric opposition and would presumably strive to shy away from this situation by greater twisting of the molecular framework.

Intramolecular Trapping of 3-Norcaren-7-ylidenes. In this section we record the transformations of carbenoids such as **60** which are of interest in connection with elaboration of the multiply functionalized tricyclo[4.1.0.0^{2,7}]hept-3-ene ring system. The previous report that reaction of dibromide **59** with



cold ethereal methyllithium produced **61** in only 1–4% yield was at first puzzling since stereochemical factors seemed entirely favorable.[30] But we, like Klummp and Vrielink, have not achieved improved conversion to this olefin. The intermediacy of "foiled carbene" **62** was invoked by the Dutch group to account for the misdirected reaction, but this rationalization did not appeal to us, Cursory inspection reveals that C–H$_\alpha$ insertion in **60b** must occur at an allylic site. But the proximate π bond would not be expected to promote such attack if inductive effects on C–H bond nucleophilicity are of paramount importance. Given that the deactivating effects of α-methoxyl substitution provide serviceable analogy.[8] then intramolecular capture within **60b** might be inhibited by the electron-withdrawing olefinic moiety to the point where other possible carbene annihilation schemes operate preferentially. A fused cyclopropane ring, known to possess less electron-withdrawing capability than vinyl,[31] has been shown above not to inhibit insertion into C–H$_\alpha$ bonds. The isolation of small amounts of **61** suggests that the detectable limit of such competitive rate retardation might possibly have been realized in **60b.**[32]

If this assumption is correct, one would expect that positioning of one or two methyl groups at the available cyclopropyl bridge positions would serve to increase on a relative basis the level of C–H$_\alpha$ insertion. In actuality, the chemical reactivities of **63** and **66** indicate again that such alkyl substitution also

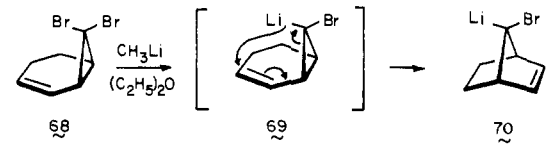


suitably predisposes these unsaturated molecules for greater bicyclobutane production. In the case of the monomethyl derivative, there was formed a 3:1 mixture of **64** and **65,** isolation of which was realized in 50% combined yield subsequent to preparative VPC separation and purification. Comparable treatment of **66** also proceeded very smoothly to give **67** (40% after VPC isolation). The structures of the three tricyclo[4.1.0.0^{2,7}]hept-3-enes follow directly from their ^1H NMR spectra (see Experimental Section) and their product-forming behavior when subjected to Ag^+-catalyzed rearrangement.[11b] The "steering effect" of the $-CH_3$ group on the carbenoid insertion pathways available to **63** again causes C$_2$–H$_\alpha$ attack to dominate.

Concluding Remarks. To test consequences of methyl substitution upon the regioselectivity and efficiency of intramolecular carbenoid capture, recourse was made to two different criteria. In the first of these, which was necessarily restricted to 7-norcaranylidenes, $-CH_3$ was appended to the methylene carbons comprising the six-membered ring in all four possible stereochemical and positional arrangements. As a consequence of these structural variations, it proved possible to identify two dominant reactivity patterns. In those conformations endowed with axially disposed H$_\alpha$ and β-CH_3 substituents as in D and E, insertion into the methyl group operates exclusively. In our opinion, these findings attest to the enhanced reactivity of carbenoids when sterically congested. In those conformations where the methyl group is equatorially oriented, insertion into the geminal C–H bond, irrespective of its α or β relationship, is markedly improved. Such reactivity patterns are believed to reflect in large part the positive inductive contributions of $-CH_3$ to the nucleophilicity of the neighboring C–H bond.

The second structural modification was to substitute the bridge positions. In the several unsymmetrical monomethyl examples studied (in all three series), the product distributions reflected a decided preference for insertion into the proximal axial C$_2$–H$_\alpha$ bond. The rationalization advanced by us is based on steric arguments and focuses attention on that conformational twisting required to relieve those nonbonded interactions with $-CH_3$ which have developed. The distance separating the carbenic center from C$_2$–H$_\alpha$ is diminished as a result (see C), this proximity fostering preferential reaction at the C$_2$ site.

A fused cyclopropane ring strikingly improves the efficiency of the cyclization pathway which leads to bicyclobutane formation, a feature which arises as the likely result of improved conformational factors (possible increased flattening of the central ring, for example)[29b] and nondeleterious electronic effects. In this latter aspect, a double bond appears to be decidedly unfavorable for intramolecular reaction. Unfortunately, it is not possible to assess these apparent shortcomings in the isomeric dibromide example **68** owing to the facility with which its carbenoid (**69**) undergoes rearrangement to **70.**[33]



Experimental Section

All boiling points are uncorrected. Melting points were obtained on a Thomas-Hoover capillary apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. ^1H NMR spectra were recorded on Varian A-60A, T-60, and HA-100 instruments as well as a Jeolco MH-100 spectrometer. Fourier spectra (both carbon and proton) were obtained on a Bruker HX-90 instrument. Apparent splittings are given. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Combustion analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was carried out with the aid of a Varian Aerograph A-90P3 chromatograph equipped with a

thermal conductivity detector, while analytical determinations were performed on a Hewlett-Packard HP5750 research gas chromatograph equipped with a flame ionization detector and Model HP3370A electronic integrator.

***syn*- and *anti*-7,7-Dibromo-1,4-dimethylnorcarane (18b and 33b).** A solution of 8.14 g (0.074 mol) of 1,4-dimethylcyclohexene in 25 mL of pentane was added to a magnetically stirred suspension of potassium *tert*-butoxide (16.8 g, 0.15 mol) in pentane (100 mL) which was precooled and maintained at 0 °C. A solution of bromoform (38.0 g, 0.15 mol) in 100 mL of pentane was slowly added to this suspension while maintaining the temperature at 0 °C. Upon completion of the addition, the mixture was stirred at room temperature for 5 h and hydrolyzed by the addition of water (50 mL). The separated organic layer was washed with water, dried, and concentrated. Distillation of the residue afforded 7.90 g (38%) of a 60:40 mixture (^{1}H NMR analysis) of the isomeric dibromides **18b** and **33b** with **18b** predominating (bp 99–101 °C at 0.4 mm). Preparative VPC isolation (column B, 135 °C)[34] gave a pure sample of the mixture: δ_{Me_4Si} ($CDCl_3$) 2.40–1.00 (m, including two singlets at 1.38 and 1.41, 11) and 0.86 (m, 3).

Anal. Calcd for $C_9H_{14}Br_2$: C, 38.32; H, 5.01. Found: C, 38.71; H, 4.98.

Carbenoid Cyclization of 18b/33b. A 5.0-g (0.017 mol) sample of the dibromide mixture (60:40) in 75 mL of anhydrous ether was precooled to −20 °C and maintained at approximately that temperature under a nitrogen atmosphere during the dropwise addition of an ethereal solution of methyllithium (10 mL of 1.82 M). Upon completion of the addition, the reaction mixture was stirred at room temperature for 1 h, cooled to 5 °C, and treated cautiously with water (25 mL). The separated organic layer was washed with brine, dried, and carefully concentrated. Flash distillation afforded 1.67 g (76%) of a clear oil, VPC analysis of which (column A, 80 °C)[34] showed four components to be present in the ratio 6:50:28:16.

The minor component was identified as 3,6-dimethyltricyclo[4.1.0.0^{3,7}]heptane (**21b**): δ_{Me_4Si} (C_6D_6) 2.20–1.15 (m, 8), 1.12 (s, 3), and 1.08 (s, 3); *m/e* 122.1097 (calcd 122.1095).

Anal. Calcd for C_9H_{44}: C, 88.45; H, 11.55. Found: C, 88.27; H, 11.82.

The major component was identified as *syn*-1,4-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**20**): δ_{Me_4Si} (C_6D_6) 2.24–2.10 (m, 2), 1.68–1.30 (m, including singlet at 1.38, 5), 1.10–0.80 (m, 6), and 0.60–0.32 (m, 1); *m/e* 122.1097 (calcd 122.1095).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.59; H, 11.53.

That component comprising 28% of the reaction mixture was formulated as 2,5-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**37b**): δ_{Me_4Si} (C_6D_6) 2.20–2.00 (m, 1), 1.60–1.20 (m, 7), 0.97 (s, 3), and 0.90 (d, J = 6 Hz, 3); *m/e* 122.1097 (calcd 122.1095).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.08; H, 11.68.

The remaining component (16%) was identified as 2-methyltricyclo[3.2.1.0^{2,7}]octane (**36b**); δ_{Me_4Si} (C_6D_6) 1.92–1.48 (m, 7), 1.48–1.18 (m, 2), 1.02 (s, 2), and 0.84 (s, 3); *m/e* 122.1097 (calcd 122.1095).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.40; H, 11.58.

Methylation of 4-Methyltricyclo[4.1.0.0^{2,7}]heptane (20a). Tetramethylethylenediamine (TMEDA, 250 μL) dissolved in 5 mL of pentane was added under nitrogen to a magnetically stirred solution of *n*-butyllithium (2 mL of 2.4 M) in hexane at 5 °C. A solution of **20a** (195 mg, 1.60 mmol) in 10 mL of pentane was slowly introduced, and the resulting solution was stirred overnight at room temperature. An additional 10 mL of pentane was added, the solution was cooled again to 5 °C, and 300 μL of methyl iodide dissolved in 5 mL of pentane was slowly admixed. After 15 min, 20 mL of water was added. The organic layer was washed with saturated copper sulfate solution and brine prior to drying. Concentration followed by flash distillation afforded a mixture of **20b** and **22** in quantitative yield. VPC isolation (column C, 50 °C)[34] afforded an analytically pure mixture of these hydrocarbons.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.23; H, 11.70.

Injection on column D[34] (110 °C) revealed two peaks of approximately equal intensity. One proved identical with **20b** (VPC and ^{1}H NMR) while the other was identified as *anti*-1,4-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**22**): δ_{Me_4Si} (C_6D_6) 2.20–1.96 (m, 2), 1.60–1.30 (m, including singlet at 1.43, 8) and 1.00–0.82 (m, including doublet, J = 7 Hz, at 0.92, 4); *m/e* 122.1097 (calcd 122.1095).

Comparable analysis of the cyclization mixture from **18b/33** showed no detectable amounts of **22.**

Ag(I)-Promoted Rearrangement of 20b. A 70.8-mg sample of **20b** (>98% purity) was dissolved in 220 μL of dry benzene and treated via syringe at room temperature with 220 μL of 0.2204 M silver perchlorate in benzene. After being heated at 40.0 °C for 12.5 h, the reaction mixture was quenched by addition of saturated brine. VPC analysis (column I, 75 °C)[34] showed three components to be present in the ratio of 28:21:51. Preparative VPC (column J, 100 °C)[34] afforded the individual hydrocarbons in a pure state.

The major product was found to be *exo*-3,6-dimethylbicyclo[3.2.0]hept-6-ene (**23**) as prepared earlier admixed with its endo isomer by Zon[14a] and differentiated stereochemically in subsequent experiments described below.

The minor product was determined to be a mixture of the 1-ethylidene-5-methylcyclohex-2-enes **25** and **26.** Injection on a silver nitrate column (column K, 50 °C)[34] resulted in their separation. The ratio of **25:26** (identified from subsequent synthesis) proved to be 4:7.

The final product was identical with an authentic sample of 2,6-dimethylcyclohepta-1,3-diene (**24**) (^{1}H NMR comparison).

Independent Synthesis of the 1-Ethylidene-5-methylcyclohex-2-enes 25 and 26. Ethyltriphenylphosphonium iodide (12.55 g, 0.030 mol) was slurried in 100 mL of dry tetrahydrofuran under nitrogen and 16 mL of 2.2 M *n*-butyllithium in hexane (0.035 mol) was slowly added. To the resulting red solution was cautiously introduced 1.52 g (0.014 mol) of 5-methyl-2-cyclohexenone[35] in 15 mL of tetrahydrofuran and the mixture was heated at reflux for 5.5 h. The cooled mixture was diluted with 75 mL of pentane, filtered into a separatory funnel, washed three times with brine, and dried. After concentration and flash distillation, 0.20 g (12%) of a 1:2 mixture of **25** and **26** was isolated by preparative VPC (column L, 130 °C).[34]

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.66; H, 11.61.

Separation of the individual isomers was also accomplished on column K.[34]

For **25:** δ_{Me_4Si} (C_6D_6) 6.08 (d, J = 9 Hz, 1), 5.70–5.40 (m, 1), 5.28 (q, J = 6 Hz, 1), 2.60–2.20 (m, 2), 2.20–1.40 (m, including doublet, J = 6 Hz, at 160, 6), and 0.92 (d, J = 5 Hz, 3); *m/e* 122.1097 (calcd 122.1095).

For **26:** δ_{Me_4Si} (C_6D_6) 6.40 (d, J = 10 Hz, 1), 5.78–5.40 (m, 1), 5.10 (q, J = 10 Hz, 1), 2.40–1.50 (m, including doublet, J = 8 Hz, at 1.60, 8), and 0.84 (d, J = 6 Hz, 3); *m/e* 122.1097 (calcd 122.1095).

Independent Synthesis of Bicycloheptene 23. Ethereal methyllithium (30 mL, 1.7 M, 0.051 mol) was added to a solution of diisopropylamine (5.15 g, 0.051 mol) in 100 mL of tetrahydrofuran. This solution was cooled to −78 °C and 5.0 g (0.051 mol) of 2-methylcyclopentanone was admixed. This mixture was stirred at −78 °C for 30 min under nitrogen prior to treatment with a solution of phenylselenyl bromide (formed from 4.0 g of bromine and 7.8 g diphenyl diselenide) in 50 mL of tetrahydrofuran.

After being warmed to room temperature, the reaction mixture was poured into a saturated sodium bicarbonate solution and extracted with methylene chloride. The total volume of methylene chloride was increased to 400 mL prior to addition of 8.5 g of pyridine. At 0 °C, 70 g of 50% hydrogen peroxide was introduced *very* cautiously. After being stirred for 30 min at room temperature, the organic layer was washed with acid and brine before drying. Concentration and flash distillation afforded 2.0 g (41%) of **28.**

Propyne (25 mL) was dissolved in 500 mL of cold benzene and placed in a 650-mL Pyrex immersion well. A solution of **28** (2.0 g) in 50 mL of benzene was added and the solution was irradiated for 20 h through quartz with a 450-W Hanovia lamp. The benzene was evaporated and the residue was flash distilled to yield a mixture of ketones isomeric with **29**, *m/e* 136.0890 (calcd 136.0888).

A 250-mg sample of the ketone mixture was dissolved in 10 mL of ethylene glycol. Potassium hydroxide (1.5 g) was added, followed by 1.0 mL of hydrazine hydrate. This mixture was heated at the reflux temperature for 3 h while water distilled from the solution. The volatiles were distilled into a water trap and extracted with pentane, dried, and concentrated. VPC analysis (column G, 60 °C)[34] showed the product to be homogeneous and identical with **23** as obtained from the Ag^+-catalyzed rearrangement of **20b** (VPC and ^{1}H NMR).

7,7-Dibromo-3,3-dimethylnorcarane (38a). A solution of 7.03 g (0.064 mol) of 4,4-dimethylcyclohexene in 25 mL of pentane was added to a magnetically stirred suspension of 8.0 g (0.071 mol) of

potassium *tert*-butoxide in pentane (100 mL) which was precooled and maintained at 0 °C. A solution of 20.0 g (0.079 mol) of bromoform in 100 mL of pentane was slowly introduced to this suspension while maintained at 0 °C. Upon completion of the addition, the mixture was stirred at room temperature for 5 h and hydrolyzed by the addition of water (50 mL). The separated organic layer was washed with water, dried, and concentrated. Distillation afforded 11.39 g (63%) of **38a**, bp 105 °C (0.75 mm). Preparative VPC purification (column B, 130 °C)[34] gave an analytical sample: δ_{Me_4Si} ($CDCl_3$) 2.30–1.70 (m, 4), 1.60–1.00 (m, 4), 0.83 (s, 3), and 0.81 (s, 3); *m/e* 279.9467 (calcd 279.9463).

Anal. Calcd for $C_9H_{14}Br_2$: C, 38.32; H, 5.01. Found: C, 38.50; H, 5.12.

Cyclization of 38a. Treatment of **38a** (2.0 g, 0.007 mol) dropwise with 5 mL of 1.6 M ethereal methyllithium (0.008 mol) at −20 °C as described above yielded 780 mg (90%) of a clear oil after flash distillation. VPC analysis (column A, 70 °C)[34] showed two components to be present in the ratio of 1:10.

The major product was identified as 5-methyltricyclo[3.2.1.$0^{2,7}$]-octane (**41a**); δ_{Me_4Si} (C_6D_6) 2.00–1.70 (m, 2), 1.60–1.40 (m, including singlet at 1.44, 4), 1.35–1.08 (m, 4), 0.83 (s, 3), and 0.80–0.50 (m, 1); *m/e* 122.1097 (calcd 122.1095).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.34; H, 11.65.

The minor product was determined to be 3,3-dimethyltricyclo[4.1.0.$0^{2,7}$]heptane (**42a**): δ_{Me_4Si} (C_6D_6) 2.20 (m, 1), 1.96 (m, 1), 1.60–1.20 (m, 4), and 1.20–0.80 (m, 8); *m/e* 122.1097 (calcd 122.1095).

7,7-Dibromo-1,4,4-trimethylbicyclo[4.1.0]heptane (38b). 1,4,4-Trimethylcyclohexene (10.9 g, 0.088 mol) was treated with 12 g (0.100 mol) of potassium *tert*-butoxide and 10 mL of bromoform in 100 mL of pentane at 0 °C in the previously described manner. The usual workup, followed by distillation, gave 14.3 g (50.3%) of **38b**: bp 110 °C (1.0 mm); δ_{Me_4Si} ($CDCl_3$) 2.00–1.45 (m, including singlet at 1.45, 8), 1.45–0.90 (m, 2), 0.88 (s, 3), and 0.82 (s, 3).

VPC isolation (column E, 130 °C)[34] gave an analytically pure sample.

Anal. Calcd for $C_{10}H_{16}Br_2$: C, 40.54; H, 5.47. Found: C, 40.69; H, 5.52.

Cyclization of 38b. The reaction of **38b** (4.0 g, 0.014 mol) with excess methyllithium at 0 °C was carried out in the usual way. Flash distillation yielded 1.61 g (84%) of a clear oil, VPC analysis (column A, 80 °C)[34] of which showed two components to be present in a 45:55 ratio.

The minor component was identified as 2,5-dimethyltricyclo[3.2.1.$0^{2,7}$]octane (**41b**): δ_{Me_4Si} ($CDCl_3$) 2.00–1.60 (m, 4), 1.40 (m, 4), 1.30–1.00 (m, 2), 0.92 (s, 3), and 0.90 (s, 3); *m/e* 136.1253 (calcd 136.1252).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.22; H, 11.98.

The major component was found to be 2,5,5-trimethyltricyclo[4.1.0.$0^{2,7}$]heptane (**42b**): δ_{Me_4Si} ($CDCl_3$) 2.00 (m, 1), 1.50–1.20 (m, 4), 1.20–1.00 (m, including singlet at 1.05, 5), and 0.81 (s, 6); *m/e* 136.1253 (calcd 136.1252).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.23; H, 11.95.

Tetracyclo[5.1.0.$0^{3,5}$.$0^{2,8}$]octane (46). Dibromide **45** (3.0 g, 0.011 mol)[20] was treated dropwise with 9 mL of 1.7 M ethereal methyllithium (0.015 mol) at −20 °C in the predescribed manner. After the usual workup, flash distillation yielded 1.1 g (91%) of an oil, VPC analysis (column G, 70 °C)[34] of which showed it to be principally one component of >95% purity: δ_{Me_4Si} (C_6D_6) 2.70–2.50 (m, 1), 2.20 (m, 1), 1.84–1.44 (m, 2), 1.32–1.08 (m, 2), and 0.60–0.16 (m, 4); *m/e* 106.0784 (calcd 106.782).

Anal. Calcd for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.64; H, 9.64.

Ag(I)-Catalyzed Rearrangement of 46. To a 10-mg sample of **46** dissolved in 300 μL of benzene was added 200 μL of a 0.2213 M solution of $AgClO_4$ in anhydrous benzene. The resulting solution was heated at 40.0 °C for 48 h prior to the addition of brine. VPC analysis of the organic layer (column G, 70 °C)[34] revealed total conversion of starting material to a single substance of longer retention time. From the solution, a clear oil was isolated whose ^1H NMR spectrum was consistent with **47** and whose IR spectrum was identical with that of 2,3-homotropilidene.[21]

Lewis Acid Catalyzed Rearrangement of 46. A 257.5-mg sample of **46** was dissolved in 1.0 mL of ether to which was added 0.1 mL of boron trifluoride etherate. After 2 h at room temperature, the progress of reaction was arrested by pouring into saturated sodium bicarbonate solution. The organic layer was separated, dried, concentrated, and flash distilled to yield 165.7 mg of a clear oil (64.4% recovery). VPC analysis (column G, 70 °C)[34] showed the oil to consist of *anti*-bishomobenzene (**48**, 40% IR comparison),[22,23] recovered starting material (23%), and a complex mixture of several other minor products from which **48** could be easily separated.

3-Methylbicyclo[4.1.0]hept-3-ene (51). 2,5-Dihydrotoluene (25 g, 0.266 mol) was dissolved in 25 mL of dichloromethane and 1 equiv of *m*-chloroperbenzoic acid in ether was added. After being stirred overnight, the solution was treated with 25 mL of water. The organic phase was washed with saturated sodium bicarbonate solution, dried, and evaporated. The residue was taken up in ether and excess lithium aluminum hydride was added. After 6 h at the reflux temperature, saturated sodium sulfate solution was added dropwise with cooling. The organic layer was washed with base, dried, and evaporated to leave a residue which was taken up in ether and added to 40 g of zinc–copper couple. Excess methylene iodide was introduced and after 24 h at the reflux temperature the mixture was cooled and treated cautiously with acetic acid (dropwise). The organic layer was washed several times with base, dried, and concentrated. This residue was dissolved in 200 mL of pyridine to which was added 60 g of *p*-toluenesulfonyl chloride. After 48 h at the reflux temperature, the solution was cooled and 500 mL of 10% sulfuric acid was added. The solution was extracted with ether (3 × 150 mL) and the combined organic layers were dried and distilled. There was obtained 2.88 g (10% overall) of **51.** Preparative VPC (column G, 70 °C)[34] provided the analytical sample: δ_{Me_4Si} (C_6D_6) 5.15 (m, 1), 2.40–2.10 (m, 4), 1.53 (br s, 3), 1.00 (m, 2), 0.60–0.30 (m, 1), and 0.30–0.00 (m, 1); *m/e* 108.0941 (calcd 108.0939).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.94; H, 11.02.

Preparation and Cyclization of 52. In the predescribed manner, 2.88 g (0.027 mol) of **51** was dissolved in pentane (50 mL) and treated with 3.0 g (0.027 mol) of potassium *tert*-butoxide and 8.0 g (0.032 mol) of bromoform at 0 °C. The residue isolated from the customary workup was dissolved in ether (75 mL) and cyclized by treatment with excess ethereal methyllithium at 0 °C. Workup and flash distillation gave a clear oil, VPC analysis (column H, 70 °C)[34] of which showed two peaks in the ratio of 5:1. The major component was identical with **53** as prepared below (VPC and ^1H NMR), while the minor constituent was formulated as 7-methyltetracyclo[5.1.0.$0^{3,5}$.$0^{2,8}$]octane (**54**); δ_{Me_4Si} (C_6D_6) 2.63 (q, J = 3 Hz, 1), 1.70–1.50 (m, 2), 1.35–1.15 (m, 2), 0.93 (s, 3), and 0.90–0.20 (m, 4); *m/e* 120.0941 (calcd 120.0939).

Methylation of 46. A 1.12-g (0.011 mol) sample of **46** was metalated at 0 °C with *n*-butyllithium and TMEDA in the predescribed manner and subsequently treated with excess methyl iodide. The usual workup afforded 950 mg (80%) of a clear distillate. VPC analysis (column G, 70 °C)[34] indicated that two products had formed in the ratio of 1:3.5.

The minor component was shown to be *syn*-1-methyltetracyclo[5.1.0.$0^{3,5}$.$0^{2,8}$]octane (**53**): δ_{Me_4Si} (C_6D_6) 2.53 (m, 1), 1.98 (m, 1), 1.67 (m, 2), 1.35 (s, 3), 0.95 (m, 2), 0.60 (m, 2), and 0.20 (m, 1); *m/e* 120.0941 (calcd 120.0939).

The major product was identified as *anti*-1-methyltetracyclo[5.1.0.$0^{3,5}$.$0^{2,8}$]octane (**55**): δ_{Me_4Si} (C_6D_6) 2.59 (q, J = 4 Hz, 1), 2.00 (m, 1), 1.67 (m, 2), 1.48 (s, 3), 0.90 (m, 2), and 0.70–0.30 (m, 3); *m/e* 120.0941 (calcd 120.0939).

Anal. (**53**/**55** mixture). Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.70; H, 10.22.

Cyclization of 56. Dibromide **56** (2.4 g, 0.008 mol)[29b] was treated with 6 mL of 1.8 M ethereal methyllithium (0.013 mol) at 0 °C in the predescribed manner. Flash distillation as before furnished 1.0 g (85%) of a clear oil. VPC analysis (column F, 150 °C)[34] showed two peaks to be present in a ratio of 3:1. The major product was identified as *syn*-1,4,4-trimethyltetracyclo[5.1.0.$0^{3,5}$.$0^{2,8}$]octane (**57**): δ_{Me_4Si} (C_6D_6) 2.25 (q, J = 4 Hz, 1), 1.90 (m, 1), 1.75–1.40 (m, 2), 1.37 (s, 3), 1.23 (s, 1), 1.10 (s, 3), 0.95 (s, 3), and 0.80–0.00 (m, 2); *m/e* 148.1255 (calcd 148.1252).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.91; H, 10.80.

The minor component was determined to be 4,4,7-trimethyltetracyclo[5.1.0.$0^{3,5}$.$0^{2,8}$]octane (**58**): δ_{Me_4Si} (C_6D_6) 2.50–2.10 (m, 1),

1.60–1.30 (m, 2), 1.38 (s, 1), 1.25 (s, 3), 1.13 (s, 1), 1.03 (s, 3), 1.00 (s, 3), and 0.70–1.10 (m, 2); *m/e* 148.1255 (calcd 148.1252).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.85; H, 11.09.

Cyclization of 63. A solution of 9.4 g (0.10 mol) of 2,5-dihydrotoluene in 50 mL of pentane was added to magnetically stirred suspension of 11.2 g (0.10 mol) of potassium *tert*-butoxide in pentane (100 mL) which was precooled and maintained at 0 °C. A solution of 25.3 g (0.10 mol) of bromoform in 100 mL of pentane was slowly introduced to this suspension while maintained at 0 °C. Upon completion of the addition, the mixture was stirred at room temperature for 5 h and hydrolyzed by the addition of water (100 mL). The separated organic layer was washed with water, dried, and concentrated. Distillation afforded 13.6 g of **63:** bp 59 °C (0.2 mm); δ_{Me_4Si} ($CDCl_3$) 5.50 (m, 2), 2.70–2.00 (m, 5), and 1.45 (s, 3).

Dibromide **63** (5.0 g, 0.019 mol) was dissolved in ether (75 mL) at −78 °C, treated with excess methyllithium in the usual manner, and allowed to warm to room temperature. Flash distillation gave 0.9 g (50%) of colorless liquid, VPC analysis (column H, 60 °C)[34] of which revealed the presence of two components in a 3:1 ratio. The major constituent was identified as 1-methyltricyclo[4.1.0.$0^{2,7}$]hept-3-ene (**64**): δ_{Me_4Si} ($CDCl_3$) 6.00–5.70 (m, 1), 5.40–5.00 (m, 1), 2.40–2.17 (m, 1), 2.17–1.85 (m, 3), 1.57 (s, 3), and 1.33 (t, J = 3 Hz, 1); *m/e* 106.0784 (calcd 106.0782).

Anal. Calcd for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.14; H, 9.57.

The minor product was found to be 6-methyltricyclo[4.1.0.$0^{2,7}$]-hept-3-ene (**65**): δ_{Me_4Si} ($CDCl_3$) 6.10–5.70 (m, 1), 5.55–5.20 (m, 1), 2.35–2.10 (m, 1), 2.05–1.90 (m, 2), 1.66 (d, J = 3 Hz, 2), and 1.11 (s, 3); *m/e* 106.0784 (calcd 106.0782).

Anal. Calcd for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.34; H, 9.53.

1,6-Dimethyltricyclo[4.1.0.$0^{2,7}$]hept-3-ene (67). Dibromide **66** (9.0 g, 0.032 mol)[36] was treated with 25 mL of 1.8 M ethereal methyllithium (0.045 mol) in the usual manner at 0 °C. Flash distillation produced 1.3 g (40%) of a clear oil. VPC isolation (column G, 70 °C)[34] gave an analytically pure sample of **67:** δ_{Me_4Si} ($CDCl_3$) 6.10–5.70 (m, 1), 5.50–5.15 (m, 1), 2.15–1.80 (m, 3), 1.52 (s, 3), 1.33 (d, J = 2 Hz, 1), 1.08 (s, 3); *m/e* 120.0941 (calcd 120.0939).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.97; H, 10.20.

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