Regiospecificity of Cyclopropylidene C–H Insertion Reactions within [*m.n.*1]Propellane Frameworks[1]

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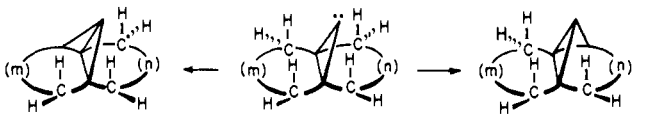
Abstract: Dibromocyclopropanes, which form an integral part of [*m.n.*1]propellanes, undergo smooth conversion to the carbenoid (quite likely an epimeric α-haloalkyllithium mixture) when treated with methyllithium. The ensuing cyclizations to bicyclo[1.1.0]butane-type products are regiospecific, the relative reactivity order of the C_α–H bonds being cyclopentyl > norcaranyl ~ 1-tetralyl > cyclohexyl > cyclohexenyl. A mechanism involving loss of lithium bromide from either carbenoid isomer with capability of leading to the same insertion product is presented. The regiospecificity appears to be determined by relative proximity of the cyclopropylidene to the neighboring C_α–H bond and the nucleophilicity of the latter. Through Ag^+-promoted isomerization, the cyclization products are isomerized to ring-expanded dienes. This added reaction has served conveniently as a means of establishing by chemical methods the course of the carbenoid insertion. More generally, the two-step sequence represents a simple method for the regiospecific insertion of a carbon atom (without attached hydrogens) into a bi- or tricyclic framework with concomitant introduction of added unsaturation.

One of the most important methods for elaborating bicyclo[1.1.0]butanes is via alkyllithium-promoted cyclization of *gem*-dihalocyclopropanes.[3] The resulting intramolecular insertion into proximate C_α–H bonds is regarded as evidence for cyclopropylidene intervention.[4,5] These processes are stereospecific (retention of configuration) and necessarily involve triangular transition states[6] rather than the linear activated complexes deemed more favorable on theoretical grounds.[7] For simple cyclopropylidenes, C–H insertion has been demonstrated to follow the reactivity order tertiary > secondary > primary[8–11] typical of carbenoid reactions,[12] although at least one exception has been noted (caused by alternative steric crowding).[13] In more rigid systems such as 7-norcaranylidenes, the product-forming step is recognized to be highly sensitive to prevailing conformational and substituent effects.[14,15] Enhanced stabilization of the first-formed lithiobromocyclopropane intermediates by appropriately positioned heteroatoms has also been encountered.[16,17]

In conformationally well-defined cyclopropylidene systems, only those structures which are capable of projecting nearby C_α–H bonds into axial orientations will deliver bicyclobutane products.[15a,b] Also, if more than one C_α–H unit can attain this geometric relationship, carbenoid attack occurs preferentially at the more nucleophilic of these bonds.[15] Such behavior is believed to be the consequence of an early transition state profile which is minimally affected by product stability considerations.[18]

The present investigation was designed to gain insight into certain more subtle discriminatory properties of cyclopropylidenes. By incorporating the carbenoid center into an [*n.n.*1]propellane framework (**1**, the carbene formulation is



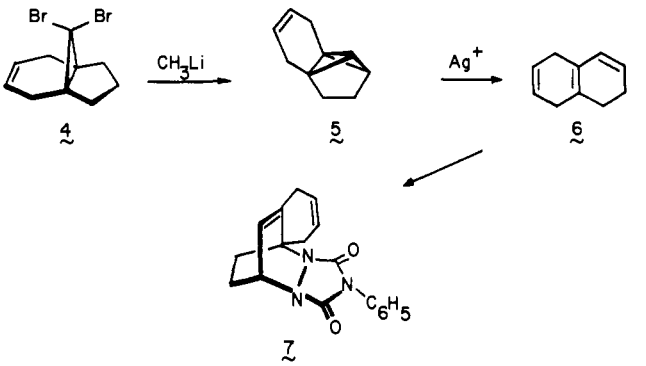
2 **1** **3**

shown for convenience only; two epimeric carbenoids are possible), two pairs of chemically distinctive adjoining C_α–H bonds are capable of attaining the required axial relationship. However, their proximity to the reaction center will be slightly different, as dictated by the nature of *m* and *n* ($m \neq n$). At issue, therefore, is the question of the degree to which *small* alterations in internuclear distance, as well as C–H bond nucleophilicity, will affect the regiochemistry of intramolecular carbenoid capture. This topic has broad implications throughout carbene chemistry.

As will be demonstrated, tetracyclic ring formation is strikingly *regiospecific*. In addition, the present results illustrate methodology for expanding one of the two rings of a bicyclic structure by one carbon atom, with concomitant introduction of added unsaturation. In the ensuing paper,[19] we apply such chemistry to bisbicyclobutane synthesis and illustrate the feasibility of double ring expansion, in particular by means of an expeditious conversion of naphthalene to heptalene.

Results

Behavior of Tricyclic Cyclopropylidenes. Following the procedure of Vogel,[20] dibromide **4** was prepared by reaction of dihydroindan with bromoform and potassium *tert*-butoxide. When treated with methyllithium in ether at 0 °C, **4** was smoothly transformed in 80% yield into a single bicyclo[1.1.0]butane derivative. That intramolecular insertion had taken place into a cyclopentane C–H bond to give **5** was sug-



4 **5** **6** **7**

gested by ^1H NMR spectroscopy and confirmed by Ag^+-promoted rearrangement.[21] Exposure to catalytic quantities of silver perchlorate in benzene afforded **6**,[22] which in turn was oxidized by 2,3-dichloro-5,6-dicyanobenzoquinone (**DDQ**) to naphthalene. Its Diels-Alder reaction with *N*-phenyltriazolinedione gave **7**.

Attack in the direction of the six-membered ring would have required insertion into one of the two allylic C_α–H bonds. Some evidence is available to suggest that such π-bond proximity may exert untoward inductive effects and thereby diminish C_α–H bond nucleophilicity.[15b,23] To remove this possible complication, **4** was hydrogenated[24] and the resulting **8** was similarly treated with methyllithium. The exclusive formation of **9**, as previously reported by Moore,[25] was observed. This structural assignment was corroborated by Ag^+-promoted

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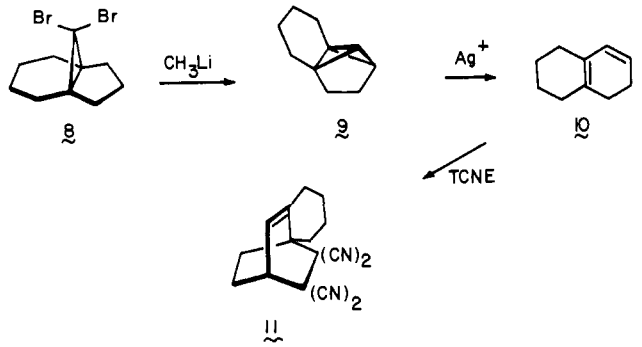


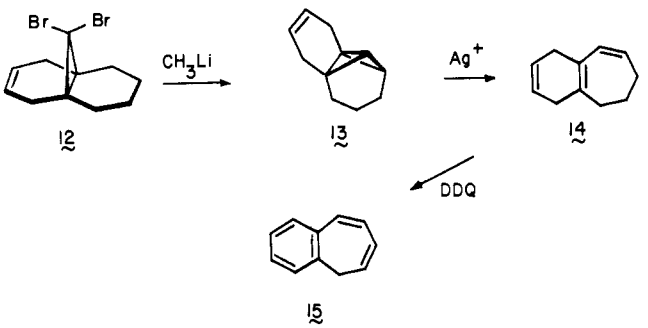
8 9 10 11

isomerization to the known diene **10**.[26] Furthermore, the spectral properties of the tetracyanoethylene (TCNE) adduct **11** were identical with those of an authentic sample, and no melting point depression was seen upon admixture with material provided by Professor Bates. Additionally, naphthalene was isolated when **10** was treated with DDQ.

As concerns both **4** and **8**, little or no carbenoid insertion into ether solvent was detected by ^{1}H NMR analysis of the unpurified products. On the other hand, utilization of *n*-butyllithium in pentane to generate the carbenoid invariably gave one or more side products formed by exchange of a bromine substituent for a butyl side chain. Although decreases in bicyclobutane yields were not always apparent, added undesirable complications in purification had to be surmounted. This procedure was, therefore, not routinely employed.

To ascertain the homogeneity of these and the subsequent cyclization products, VPC analyses were routinely carried out on all reaction mixtures both prior to and after molecular distillation. In every instance, no evidence was gained for the formation of a second bicyclobutane. These results accord with the observed homogeneity of the various Ag^+-catalyzed rearrangement products, whether obtained from crude or purified bicyclobutanes. The diminished yields noted in certain cases appear to be attributable in part to polymerization which materializes during distillation.

In the third example studied, the cyclopropylidene was forced to differentiate between a saturated and an unsaturated six-membered ring. As matters turned out, **12**[24,27] underwent cyclization to give **13** as the only isolable bicyclobutane in 56%

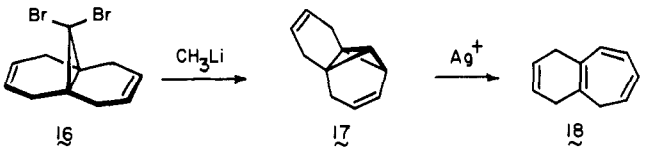


12 13 14 15

yield. The significant features of the ^{1}H NMR spectrum of **13** are the relatively narrow width of the vinylic proton multiplet (δ 5.84-5.17) and the upfield position (δ 0.91-0.79) of the "wing-proton" signal. If bicyclobutane formation had occurred α to the double bond, the pair of olefinic hydrogens should have exhibited widely different chemical shifts and appeared as a very broad multiplet (see select examples below). Additionally, the wing proton would now be allylic and subject to customary downfield shifting.

Ag^+-catalyzed isomerization of **13** led cleanly to the nonfully-conjugated triene **14**, a tetrahydrobenzotropilidene which could be readily handled. In this instance, oxidation provided the well-known **15**.

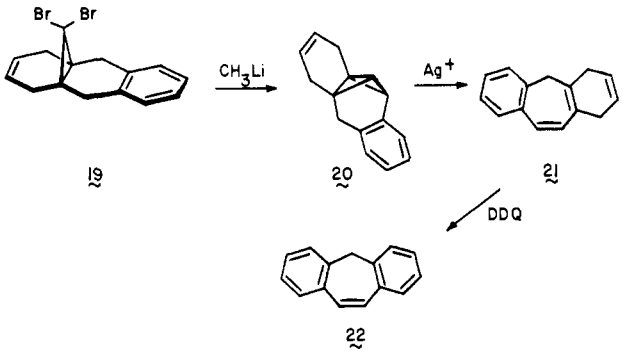
To show that tricyclic cyclopropylidenes of the [*m.n.*1]-propellane type can indeed undergo insertion into allylic C-H bonds, we treated **16**[27,28] with ethereal methyllithium at 0 °C and observed conversion to **17** in 62% distilled yield. The symmetry of **16** precludes any question of regiochemistry.



16 17 18

Nonetheless, confirmatory evidence was sought by means of the standard isomerization-dehydrogenation sequence. Clean conversion via **18** to **15** was achieved.

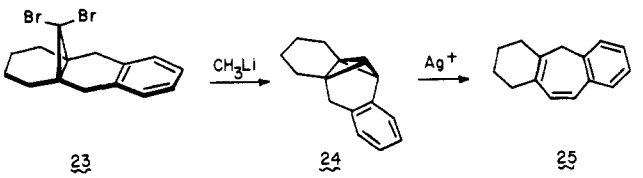
At this juncture, the relative reactivities of allylic and benzylic C_α-H bonds were assessed. Prepared by regioselective dibromocarbene addition to 1,4,9,10-tetrahydroanthracene,[29] dibromocyclopropane **19**[30] was transformed by methyllithium uniquely into **20**. This product was identified on the basis of



19 20 21 22

its subsequent rearrangement to **21** and oxidation to dibenzocycloheptatriene (**22**), the melting point,[31] infrared spectrum,[32] and ^{1}H NMR spectrum[33] of which were identical with those appearing in the literature. Had carbenoid insertion originally taken place into the cyclohexane ring, naphtho[*b*]-cycloheptatriene would have materialized instead.

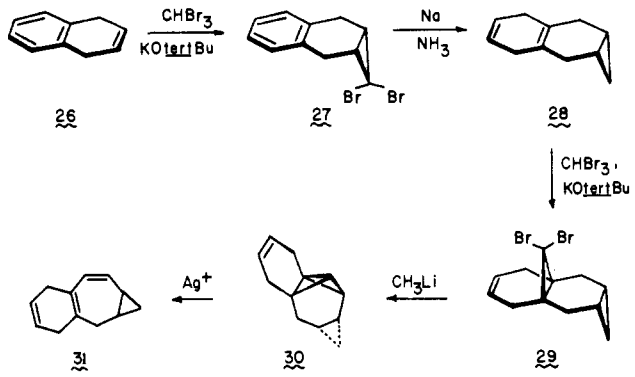
Dibromide **23**, available through catalytic hydrogenation of **19**, provided needed information concerning the preference for bicyclobutane formation in a saturated vs. a benzo-fused six-membered ring. When treated with methyllithium, **23**



23 24 25

provided a single pentacyclic product identified as **24** on the basis of its subsequent Ag^+-catalyzed rearrangement to **25**. As with **21**, DDQ oxidation of the isomerized polyolefin afforded dibenzocycloheptatriene. Clearly, the tendency in the carbenoids derived from either **19** or **23** is for exclusive benzylic C_α-H insertion.

As a direct result of the regiospecificity of these experiments, we were led to examine the chemical reactivity of the carbenoids derived from dibromide **29**. Placement of the unsubstituted cyclopropane ring on the exterior of the molecule was achieved by reaction of 1,4-dihydronaphthalene (**26**) with bromoform and potassium *tert*-butoxide. When the resulting adduct **27** was treated with sodium in liquid ammonia, simultaneous debromination and Birch reduction materialized to furnish **28**. Controlled dibromocarbene addition to **28** resulted in preferential cyclopropanation of the more highly substituted double bond and delivery of the desired **29**. Reaction of **29** with methyllithium in the conventional way served to produce only **30**, thereby indicating a marked preference for intramolecular attack at a cyclopropylcarbinyl C_α-H bond.

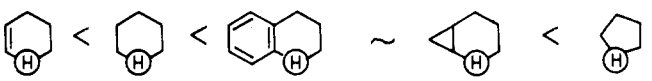


26 27 28 29 30 31

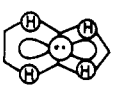
Because the ^1H NMR spectrum of **30** shows the typical narrow downfield multiplet of area 2 for the olefinic protons in a "regular" cyclohexene ring (δ 5.70-5.50) and the wing proton in a shielded environment (δ 0.30-0.10), carbenoid insertion into the unsaturated ring could be easily discounted. In an ancillary experiment, **30** was isomerized to the interesting homotropilidene **31**.

Discussion

Analysis of Cyclopropylidene Regiospecificity. The striking feature of the present findings is the exceptionally discriminative reactivity of cyclopropylidenes toward a varied selection of neighboring *axial* C_α-H bonds. Based upon the several case studies examined, it is now clear that intramolecular carbenoid insertion into cyclopentane C_α-H bonds is most efficient, while that into allylic cyclohexene C_α-H bonds is least. In fact, the following ordering of relative reactivity has been uncovered, although it is conceded that the bicyclo[4.1.0]heptyl-cyclohexyl ordering is an inferred one not supported by direct experiment.



As judged from molecular models, the axial C_α-H protons of a 6-bicyclo[3.1.0]hexylidene moiety not only find themselves in somewhat closer proximity to the carbenoid center than do the same protons in 7-norcaranylidenes, but also better aligned for overlap with the vacant electrophilic orbital of the intermediate. This phenomenon is most readily apparent when such structures are viewed from above as exemplified by **32**. The



32

emergence of more favorable σ bond canting and greater orbital proximity concisely accounts for the heightened preference for insertion into cyclopentane rings. Conversely, the inductive effect of the π bond in a cyclohexene ring can be expected to deter allylic C-H insertion if C-H bond nucleophilicity is as kinetically important as it appears to be.

In an earlier study, we demonstrated that fusion of a cyclopropane ring to C_3 and C_4 of a 7-norcaranylidene markedly improves the efficiency of the cyclization pathway leading to a bicyclo[1.1.0]butane formation.[15b,34] This phenomenon was attributed to possible added flattening of the six-membered ring and, particularly, to nondeleterious electronic influences. In this latter connection, a fused cyclopropane ring has been shown to possess less electron-withdrawing capability than a double bond.[35] Therefore, the cyclization of **29** exclusively to **30** is as expected based upon these considerations.

If the preceding assumptions are correct, one would expect a fused benzene ring to exert a less untoward effect than a double bond on neighboring C-H bond nucleophilicity. In actuality, our results indicate that benzylic C_α-H bonds are more favorably disposed for bicyclobutane production that those of allylic origin or those simply contained in saturated cyclohexane rings. The enhanced reactivity of benzylic as compared to cyclohexyl sites is believed by us to reflect the surmounting of a somewhat diminished inductive contribution to C_α-H bond nucleophilicity by conformational factors which position the C_α-H bond closer to the reaction center. Stated differently, the distance separating the carbenoid center from the C_α-H bond when benzo fusion is involved is shortened as a result of the contracted length of the C_3-C_4 bond (now a segment of the benzene ring). A comparable structural modification is present within cyclohexenyl rings, but response to carbenoid insertion is lessened because of heightened inductive π-bond withdrawal from the C_α-H bonds.

The preceding discussion has not explicitly considered carbenoid center stereochemistry as a parameter of consequence in dictating the observed regiospecificity. In this connection, Taylor and his co-workers have recently demonstrated that **33** and **35** respond entirely differently to thermolysis.

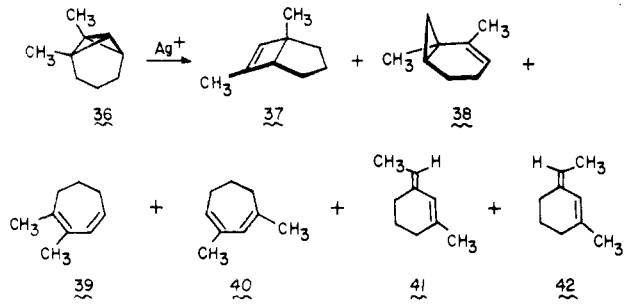
33 34 35

Whereas **33** with its exo chlorine cleanly gave the intramolecular C-H insertion product **34**, **35** preferred to react intermolecularly and to afford almost exclusively dimers and ether (solvent) insertion products.[16c] They were forced to conclude that, under their conditions, an intermediate such as a free carbene or a carbene complex having an ionized C-Cl bond had not formed reversibly.

Although stereochemical considerations are of consequence in six of the seven carbenoids examined herein, we are not aware at this time of any conformational or substituent effect that would preclude intramolecular C-H insertion by either carbenoid isomer in either of the two possible directions. If the intermediates in question are capable of conventional ring opening to an allene despite the excessive strain that would arise,[14,36] epimerization by such a mechanism could take place. However, the regiospecificity could stem as well from two other sources. In the first, the methyllithium would be required to abstract one of the bromine atoms with exceptional selectivity, such that subsequent insertion is controlled by the outcome of the halogen-metal exchange. Alternatively, both carbenoids could be formed and both could experience the ultimate loss of lithium bromide to undergo very selective C_α-H insertion without regard to stereochemical origin. It is known that α-halocyclopropyllithium reagents can be formed with reasonable stereoselectivity when neighboring stabilizing groups (e.g., ether oxygen) are present, but seemingly not otherwise.[16,37] Thus, the first criterion lacks adequate precedent and is also not intuitively satisfying.

On the other hand, the heightened selectivity of cyclopropylidenes for insertion into neighboring C-H bonds has been demonstrated previously in simpler systems.[8,15] Accordingly, we presently consider predetermined cyclopropyl carbenoid stereochemistry to be unimportant in propellane frameworks. The observed regiospecificity would appear to result from geometric factors and the ability of adjacent C_α-H bonds to supply electron density to the proximate electron-deficient carbenoid in the transition state for cyclization. The question of whether free carbenes are involved in these systems cannot be answered.[38] The most reasonable conclusion suited to our observations is that either possible carbenoid is capable of delivering the same insertion product.

Preference for Type α Silver(I)-Catalyzed Isomerization. The bicyclo[1.1.0]butane ring system which constitutes the principal structural component of **5, 9, 13, 17, 20, 24,** and **30** is known to be capable of four distinctively different Ag^+-promoted rearrangements depending upon the degree and type of substitution. These conversions to 1,3-cycloheptadienes, methylenecyclohexenes, bicyclo[3.2.0]hept-6-enes, and 2-norcarenes have been categorized as the type α, β, γ, and δ processes, respectively.[39] Although the type α transformation is most frequently seen,[21] incursion of the type γ rearrangement is generally encountered upon alkyl substitution of one or both bridgehead sites.[9] The behavior of **36** which leads chiefly to **37** (52%, note regiospecificity), as well as to **38** (8%),



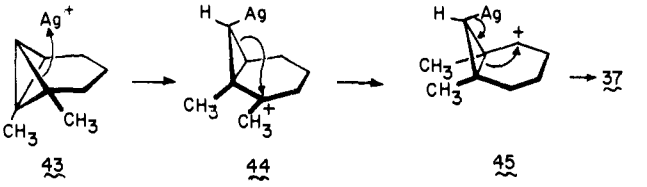
39 (10%), **40** (2%), **41** (14%), and **42** (14%), may be viewed as prototypical, although the assortment of isomeric hydrocarbons is somewhat richer than normal in this case. The available experimental evidence indicates that bicyclo[3.2.0]hept-6-ene production is initiated by attack of Ag^+ *from behind the flap* of the less sterically congested surface, at the edge bond which leads to the more stable cation (see **43,** Scheme I). Once intermediate **44** is generated, cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement ensues with its customary high stereochemiical control[40] to position the covalently bonded Ag substituent exo (**45**). At this point in the reaction manifold, the electronic alignments become such that product is formed by simple ejection of Ag^+.

A delicate balance between the steric accessibility of Ag^+ to a given edge bond and product distribution has previously manifested itself. Apparently the approach of Ag^+ to **9** and its homologues from the same direction as in **43** is less kinetically favorable. Instead, approach *to the front side of the flap* with cleavage of the identical edge bond now appears to dominate. In this reaction channel (**46,** Scheme II), the Ag atom immediately finds itself exo oriented, with the result that direct collapse with loss of the transition metal materializes (the type α pathway). Owing to the tertiary cationic nature of **47** and the customary proclivity for generating highly substituted double bonds, electronic reorganization proceeds as shown to give 1,3-cyclohexadiene (or 1,3-cycloheptadiene) product.

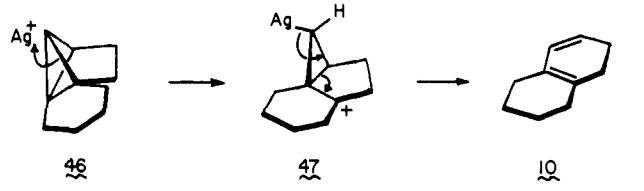
It is possible that Ag^+-catalyzed rearrangement of **20** and **24** could proceed by cleavage of the less sterically encumbered edge bond to the benzylic carbon (see **48,** Scheme III). The interaction of consequence in these examples is seemingly not whether a tertiary (**49**) or benzylic cyclopropylcarbinyl cation (**50**) develops as intermediate, but that Ag^+ approach the substrate from above the flap in both instances. Because the two intermediates are interconvertible by cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement, these pathways are difficult to distinguish. Given the fact that **5, 9, 13, 17,** and **30** uniformly appear to experience front side attack by Ag^+ (path a), it would be superfluous under normal circumstances to invoke the possibility of path b (Scheme III). However, we are not in a position to rule out a competitive situation in these examples as a consequence of the more closely balanced nature of carbocation stability in **49** and **50.**

One-Carbon Ring Expansion in Synthesis. Owing to the broad applicability of the Birch reduction and the chemo-

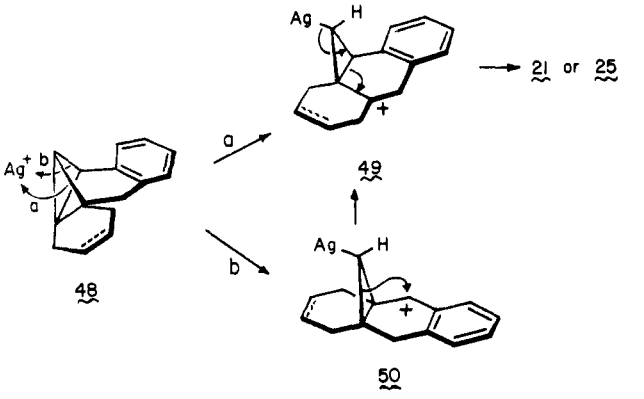
Scheme I



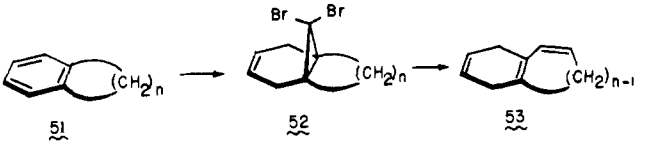
Scheme II



Scheme III



selectivity generally exhibited by dibromocarbene in adding to the more highly substituted double bond of a polyolefin, transformations of the type **51** → **52** are now commonplace.



Presently, evidence is provided that methyllithium-induced carbenoid cyclization of **52** followed by Ag^+-catalyzed rearrangement delivers **53,** the product of single carbon atom insertion (no additional hydrogens are incorporated) into the noncyclohexadienyl ring. Enlargement of that cycle results, in tandem with introduction of a second conjugated double bond. Since the carbenoid carbon is inserted between the original $-(CH_2)_n-$ bracket and central double bond, such molecules can be regiospecifically labeled with isotopic carbon if desired. Notwithstanding, simple synthetic methodology is now available for the preparation of heretofore elusive trienes of type **53.**

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with Varian T-60, Varian A-60A, and Bruker HX-90 spectrometers and referenced to tetramethylsilane; apparent splittings are given in all cases. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument and mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Preparative VPC work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

2,3,4,7-Tetrahydro-1,3a,7a-methenoindene (5). To a stirred solution of dibromide **4**[20] (2.92 g, 10 mmol) in 50 mL of dry ether was added a 1.6 M methyllithium solution (6.25 mL, 10 mmol) at 0 °C under nitrogen. After gradual warming to room temperature during 2 h, the

ethereal solution was washed with water and brine, dried, concentrated at atmospheric pressure, and flash distilled (100 °C, 0.2 mm) to yield the colorless, liquid bicyclobutane **5** (1.06 g, 80%). Preparative VPC (TCEP, 60 °C) provided the analytical sample; ^{1}H NMR (δ, $CDCl_3$) 5.63 (br s, 2 H), 2.75–2.63 (m, 1 H), 2.57–2.32 (m, 3 H), 2.26–2.17 (m, 1 H), and 1.28 (br s, 5 H); ν_{max} (film) 3020, 1650, 1435, 778, and 760 cm^{-1}; *m/e* calcd 132.0939, obsd 132.0942.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.51; H, 9.21.

1,2,5,8-Tetrahydronaphthalene (6). To a solution of unsaturated bicyclobutane **5** (300 mg, 2.27 mmol) in 10 mL of benzene was added 2 mL of 0.2 M silver perchlorate in benzene. There followed an exothermic reaction; after 1 h, the mixture was washed with brine (three times) and concentrated to yield colorless triene **6** (156 mg, 52%); ^{1}H NMR (δ, $CDCl_3$) 5.68 (br s, 4 H), 2.67 (br s, 4 H), and 2.10 (br s, 4 H).

A solution of **6** (98.6 mg, 0.75 mmol) in 5 mL of ethyl acetate was treated with *N*-phenyltriazolinedione (132 mg, 0.75 mmol) at 25 °C. The red color of the dienophile was discharged immediately, and the resulting solution was evaporated to furnish the adduct in quantitative yield. Recrystallization from ethanol provided analytically pure **7**: mp 138–139 °C; ^{1}H NMR (δ, $CDCl_3$) 7.37 (br, s, 5 H), 6.20–5.73 (br m, 3 H), 5.03–4.75 (br m, 1 H), 3.83–3.38 (br m, 1 H), 2.98–2.78 (br m, 2 H), 2.33–1.90 (br m, 3 H), and 1.65–1.30 (br m, 2 H).

Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.06; H, 5.65; N, 13.54.

Oxidation of 6 to Naphthalene. Tetrahydronaphthalene **6** (57 mg, 0.44 mmol) and dichlorodicyanoquinone (400 mg, 1.76 mmol) were refluxed in 5 mL of benzene for 12 h. The reaction mixture was filtered through a short column of alumina and the eluate was evaporated to give pure naphthalene, identified by comparison of its ^{1}H NMR spectrum with that of authentic material.

1,2,3,4,5,6-Hexahydronaphthalene (10).[26] Freshly distilled dibromide **8**[24] (3.92 g, 13.3 mmol) was dissolved in 50 mL of dry ether and stirred under argon at −23 °C during the addition (over 10 min) of an ethereal 2 M methyllithium solution (10 mL, 20 mmol). The mixture was allowed to warm to room temperature and stirred for 9 h, whereupon it was washed with water and alkaline brine, dried, and concentrated. The ^{1}H NMR spectrum of the residual oil [(δ, C_6D_6) 2.00–1.16 (m)] showed little or no ether insertion product. Without further purification, this material was dissolved in 10 mL of dry benzene and stirred for 2 h under argon with 10 mL of 2 M silver perchlorate solution in benzene. The reaction mixture was washed twice with brine, dried, carefully concentrated below 25 °C, and distilled (50 °C, 0.1 mm) to yield diene **10** (1.0 g, 56%) as a colorless liquid: ^{1}H NMR (δ, neat) 5.53 (br s, 2 H) and 2.14–1.44 (br m, 12 H).

5,6,7,8-Tetrahydro-2*H*-2,4a-ethenonaphthalene-3,3,4,4-tetracarbonitrile (11). A mixture of hexahydronaphthalene **10** (220 mg, 1.64 mmol) and tetracyanoethylene (196 mg, 1.53 mmol) in 5 mL of ethyl acetate was stirred under argon for 36 h at 25 °C and then evaporated to give a solid (380 mg, 88%). Recrystallization from chloroform–cyclohexane and sublimation (100 °C, 0.05 mm) afforded **11** as a colorless solid: mp 156.5–157.5 °C (lit.[26] mp 151–153 °C); ^{1}H NMR (δ, $CDCl_3$) 6.20 (d, J = 7 Hz, 1 H), 3.43 (d, J = 7 Hz, 1 H), and 2.60–1.40 (m, 12 H).

Oxidation of 10 to Naphthalene. Diene **10** (31 mg, 0.23 mmol) was stirred at the reflux temperature with DDQ (173 mg, 0.76 mmol) in 5 mL of benzene under argon for 10 h, then filtered through a short plug of alumina (pentane elution). Evaporation yielded naphthalene (13 mg, 44%).

1,2,3,4,5,8-Hexahydro-1,4a,8a-methenonaphthalene (13). Dibromide **12**[24,27] (3.5 g, 11.4 mmol) was stirred as a suspension in 60 mL of cold (0 °C), dry ether during the dropwise addition of 1.6 M methyllithium solution (8 mL, 12.8 mmol). After the reaction mixture was allowed to warm to room temperature with stirring for 4 h, it was washed with water and brine, dried, concentrated at atmospheric pressure, and distilled (bp 28–30 °C, 0.2 mm) to provide liquid bicyclobutane **13** (940 mg, 56%): ^{1}H NMR (δ, $CDCl_3$) 5.84–5.17 (m, 2 H), 2.93–2.83 (m, 1 H), 2.54–1.40 (m, 6 H), 1.30 (br s, 4 H), and 0.91–0.79 (m, 1 H); ν_{max} (film) 3020, 2930, 2855, 2830, 1435, 986, 915, 790, 760, and 658 cm^{-1}; *m/e* calcd 146.1095, obsd 146.1099.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 89.98; H, 9.67.

1,4,6,7-Tetrahydro-5*H*-benzocycloheptatriene (14). A solution of **13** (250 mg, 1.7 mmol) in dry benzene (5 mL) was added during 10 min to a solution of silver perchlorate (200 mg) in benzene (50 mL). After being stirred under argon for 24 h, the progress of the reaction was arrested by the addition of saturated sodium chloride solution. Concentration and flash distillation of the dried organic layer gave **14** (140 mg, 56%) as a colorless oil: ^{1}H NMR (δ, $CDCl_3$) 7.07–6.95 (m, 1 H), 6.37–6.23 (m, 1 H), 5.63 (br s, 2 H), 2.77–2.53 (m, 4 H), and 2.33–1.37 (m, 6 H); ν_{max} (film) 3020, 2925, 2850, 1490, 1445, 795, 778, 732, and 653 cm^{-1}; *m/e* calcd 146.1095, obsd 146.1098.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 89.94; H, 9.61.

Oxidation of 14 to Benzocycloheptatriene (15). A solution of **14** (100 mg) in benzene was stirred at room temperature with 200 mg of DDQ for 24 h. After filtration through a short column of alumina (pentane elution), the eluate was concentrated. The ^{1}H NMR spectrum of the residue (85 mg) was identical with that of authentic benzocycloheptatriene.

1,4,5,8-Tetrahydro-1,4a,8a-methenonaphthalene (17). A solution of unsaturated dibromide **16**[27,28] (3.04 g, 10 mmol) in 50 mL of dry ether was stirred under nitrogen at 0 °C during the addition of 1.6 M methyllithium (6.25 mL, 10 mmol). The resulting solution was allowed to warm with stirring for 2 h, washed with water and brine, dried, concentrated at atmospheric pressure, and flash distilled under vacuum to provide colorless liquid bicyclobutane **17** (890 mg, 62%). Preparative VPC purification (6 ft × 0.25 in. 10% tetracyanoethyl pentaerythritol (TCEP), 90 °C) provided the analytical sample: ^{1}H NMR (δ, $CDCl_3$) 6.13–5.20 (m, 4 H), 2.47–1.92 (m, 7 H), and 1.32–1.20 (m, 1 h); ν_{max} (film) 3025, 1643, and 1442 cm^{-1}; *m/e* calcd 144.0939, obsd 144.0942.

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.61; H, 8.62.

1,4-Dihydro-5*H*-benzocycloheptene (18). A solution of bicyclobutane **17** (100 mg, 0.7 mmol) in 10 mL of benzene was stirred with 1 mL of 0.15 M anhydrous silver perchlorate in dry benzene. After 10 min at 25 °C, the mixture was washed with brine (three times), dried, and concentrated. Preparative VPC as above (120 °C) indicated that a single volatile product had formed and provided an analytical sample: ^{1}H NMR (δ, $CDCl_3$) 6.43–5.23 (m, 6 H), 2.88 (br s, 4 H), and 2.30 (d, J = 7 Hz, 2 H); *m/e* calcd 144.0939, obsd 144.0942.

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.23; H, 8.51.

1,4,9,10-Tetrahydroanthracene and 1,4,5,8,9,10-Hexahydroanthracene. Recrystallized (ethanol) 9,10-dihydroanthracene (33.5 g, 186 mmol) dissolved in 2.8 L of tetrahydrofuran was added to 4.5 L of refluxing ammonia under argon. Several small pieces of lithium wire (2.86 g, 412 mg-atoms) were added. After stirring for 4 h, the progress of reaction was arrested by the introduction of 150 mL of ethanol (in less than 20 s) and the ammonia was allowed to evaporate. Methylene chloride was added and the organic phase was washed with water (three times) and brine, then evaporated to dryness. Crystallization of the residue from benzene removed most of the hexahydroanthracene (7.8 g, 22%) as white needles. Recrystallization of the second residue from acetone yielded white plates of the tetrahydroanthracene (20.43 g, 60%), 95% pure by ^{1}H NMR. Charge transfer chromatography[29,41] could also be used to separate the isomers, requiring considerably less adsorbent (20:1 rather than 400:1 by weight) if 5% methylene chloride–hexane was used in place of benzene–hexane.[29] However, this method was not as adaptable to scale-up.

11,11-Dibromo-1,4,9,10-tetrahydro-4a,9a-methanoanthracene (19). 1,4,9,10-Tetrahydroanthracene (10 g, 55 mmol) in 60 mL of benzene was admixed with potassium *tert*-butoxide (6.77 g, 60 mmol) in 250 mL of pentane at 0 °C under argon. Bromoform (15.3 g, 60 mmol) in 10 mL of benzene was added over 30 min. After 10 h, water was added and the mixture was filtered. The organic phase was washed with water and brine, dried, concentrated, and chromatographed on neutral alumina with benzene as eluant. The product so obtained was recrystallized from benzene to yield dibromide **19** (7.9 g, 41%), mp 139–142 °C (lit.[30] mp 148 °C), and recrystallization from acetone returned 2.37 g of tetrahydroanthracene (52% yield based on recovered starting material).

1,4,9,10-Tetrahydro-4a,9,9a-methenoanthracene (20). A 2 M methyllithium solution (10.6 mL, 21 mmol) was added dropwise to a stirred suspension of dibromide **19** (5 g, 14 mmol) in 25 mL of ether–pentane (1:1) at 15 °C under argon. After 14 h, the mixture was washed with water (twice) and alkaline brine, dried, concentrated, and distilled (110–120 °C, 0.1 mm) to give a colorless semisolid (1.56 g, 57%). VPC analysis on an inert glass column (10 ft × 0.25 in. 0.2%

SE-30, 159 °C) indicated 92% purity with indications of decomposition on the column, although the technique provided an analytical sample: ^{1}H NMR (δ, C_6D_6) 6.96-6.74 (m, 4 H), 5.76-5.34 (m, 2 H), and 3.10-1.95 (m, 9 H).

Anal. Calcd for $C_{15}H_{15}$: C, 92.74; H, 7.26. Found, C, 92.83; H, 7.29.

4,5-Dihydro-1*H*-dibenzo[*a*,*d*]cycloheptene (21). A solution of bicyclobutane **20** (300 mg, 1.54 mmol) in 2 mL of benzene was degassed and added to 200 mg of dried silver perchlorate in 20 mL of benzene. After 20 h, the tan solution was washed with alkaline brine (twice), concentrated, and distilled (110-115 °C, 0.1 mm) to give a yellow semisolid (140 mg, 47%), mp 64-71 °C. VPC analysis (3 ft × 0.25 in. 5% SE-30, 202 °C) indicated 87% purity material and provided the analytical sample: ^{1}H NMR (δ, C_6D_6) 7.16-6.78 (m, 5 H), 6.13 (d, J = 12 Hz, 1 H), 5.53 (s, 2 H), and 2.90-2.59 (m, 6 H).

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.75; H, 7.33.

2,3:6,7-Dibenzocyclohepta-2,4,6-triene (22). A slurry of **21** (30 mg, 0.15 mmol) and DDQ (35 mg, 0.15 mmol) in 2 mL of carbon tetrachloride-benzene (1:1) was agitated for 45 min. Chromatography of the entire reaction mixture on neutral alumina (pentane elution) and concentration of the eluate under reduced pressure afforded crude dibenzocycloheptatriene (15 mg, 51%). Sublimation (100 °C, 0.1 mm) and recrystallization from methanol gave product of mp 129.5-131 °C (lit.[31-33] mp 133-134 °C); ^{1}H NMR (δ, C_6D_6) 7.32-7.18 (m, 8 H), 7.00 (s, 2 H), and 3.72 (s, 2 H); ν_{max} (KBr) 3020, 808, 759, and 729 cm^{-1}.

11,11-Dibromo-1,2,3,4,5,10-hexahydro-4a,9a-methanoanthracene (23). A solution of **19** (500 mg, 1.4 mmol) dissolved in ethyl acetate (10 mL) was reduced at atmospheric pressure over 5% Pd-C catalyst (50 mg) until no further hydrogen was taken up. After filtration of the reaction mixture through a plug of glass wool, the solvent was evaporated and the residue was recrystallized from ethanol to give **23** (460 mg, 92%) as colorless needles: mp 120-125 °C; ^{1}H NMR (δ, $CDCl_3$) 7.13-6.93 (m, 4 H), 3.03-2.83 (m, 4 H), 2.03-1.67 (m, 4 H), and 1.63-0.80 (m, 4 H); ν_{max} (KBr) 3030, 2960, 2940, 2865, 1488, 1456, 1451, 1427, 1387, 956, 909, 799, and 753 cm^{-1}; *m/e* calcd 353.9620, obsd 353.9629.

1,2,3,4,9,10-Hexahydro-4a,9,9a-methenoanthracene (24). To a stirred solution of **23** (450 mg, 1.3 mmol) in dry ether at 0 °C under argon was added dropwise during 10 min a solution of methyllithium in ether (2 mL of 1.75 M, 3.5 mmol). The resulting solution was stirred at 0 °C for 1 h and at room temperature for 2 h before being quenched with water (40 mL). Extraction of the aqueous phase with ether (40 mL) was followed by washing of the combined organic layers with brine. Drying, concentration, and flash distillation of the residue gave **24** (190 mg, 77%) as a colorless oil: bp 110-115 °C (0.1 mm); ^{1}H NMR (δ, $CDCl_3$) 7.13-6.77 (m, 4 H), 3.53-3.27 (m, 1 H), 2.93-1.17 (m, 10 H), 0.80-0.67 (m, 1 H); ν_{max} (film) 3060, 3010, 2920, 2845, 1605, 1585, 1480, 1445, 1215, 1100, 972, 941, 892, 835, 755, 728, and 715 cm^{-1}; *m/e* calcd 196.1252, obsd 196.1256.

Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.71; H, 8.26.

2,3,4,5-Tetrahydro-1*H*-dibenzo[*a*,*d*]cycloheptene (25). A solution of **24** (200 mg) in dry benzene (5 mL) was added dropwise during 0.5 h to a stirred solution of silver perchlorate (300 mg) in dry benzene (20 mL). The resulting solution was stirred at room temperature for 24 h under argon and then washed with saturated sodium chloride solution (3 × 20 mL). Subsequent filtration, concentration, and flash distillation gave **25** (130 mg, 65%) as a pale yellow oil: ^{1}H NMR (δ, $CDCl_3$) 7.17-6.83 (m, 4 H), 6.77 (d, J = 11 Hz, 1 H), 6.10 (d, J = 11 Hz, 1 H), 2.85 (s, 2 H), 2.33-1.83 (m, 4 H), and 1.73-1.33 (m, 4 H); ν_{max} (film) 3060, 3005, 2925, 2880, 2850, 2830, 1600, 1487, 1450, 1433, 870, 787, and 748 cm^{-1}; *m/e* calcd 196.1252, obsd 196.1256.

Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.97; H, 8.20.

Oxidation of 25 to Dibenzocycloheptatriene (22). A solution of **25** (80 mg) in benzene (5 mL) was stirred with DDQ (150 mg) for 24 h at room temperature. The reaction mixture was filtered through a short column of alumina (pentane elution) and the eluate was concentrated and evacuated to give a colorless solid (20 mg) identified as dibenzocycloheptatriene (**22**) by comparison of ^{1}H NMR spectra. Sublimation gave a sample of mp 128-130 °C.

7,7-Dibromobenzobicyclo[4.1.0]hept-3-ene (27). A suspension of potassium *tert*-butoxide (9.52 g, 85 mmol) and 1,4-dihydronaphthalene (10 g, 77 mmol) in pentane (250 mL) was stirred at 0 °C while bromoform (21.5 g, 85 mmol) was added dropwise during 0.5 h. The resulting mixture was stirred at 0 °C for 1 h and then at room temperature for 3 h before being quenched with water (200 mL). The aqueous phase was further extracted with pentane (100 mL) and the combined organic layers were washed with saturated sodium chloride solution and dried. Concentration and distillation afforded **27** (11.2 g, 48%) as a pale yellow oil: bp 120-122 °C (0.1 mm); ^{1}H NMR (δ, $CDCl_3$) 6.92 (s, 4 H), 3.12 (m, 2 H), 2.55 (d, J = 15 Hz, 2 H), and 2.03-1.83 (m, 2 H); ν_{max} (film) 3070, 3025, 2940, 2900, 2840, 1588, 1500, 1455, 1426, 1325, 1207, 1058, 1040, 901, 789, 791, 776, 750, and 715 cm^{-1}; *m/e* calcd 299.9150, obsd 299.9157.

Dihydrobenzobicyclo[4.1.0]hept-3-ene (28). Sodium (11.5 g, 0.5 g-atom) was added in pieces to liquid ammonia (500 mL) and the resulting solution was stirred under reflux for 30 min. A solution of **27** (15 g, 0.05 mol) and *tert*-butyl alcohol (20 g, 0.27 mol) in dry ether (120 mL) was added dropwise during 0.5 h and the resulting mixture was stirred under reflux for 4 h before being quenched by the cautious addition of methanol (100 mL). After the ammonia had evaporated, water was slowly added and the solution was extracted with hexane. The extract was washed with saturated sodium chloride solution, dried, and concentrated. The resultant oil was distilled to give **28** (6.35 g, 88%) as a colorless liquid: bp 55-56 °C (0.1 mm); ^{1}H NMR (δ, $CDCl_3$) 5.63 (br s, 2 H), 2.57-2.37 (m, 4 H), 2.30-2.03 (m, 2 H), 1.97-1.50 (m, 2 H), 1.20-0.83 (m, 2 H), and 0.63-0.03 (m, 2 H); ν_{max} (film) 3030, 2930, 2875, 2835, 1495, 1452, 1439, 1016, 938, 820, 809, 744, and 657 cm^{-1}; *m/e* calcd 146.1095, obsd 146.1099.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.49; H, 9.63.

12,12-Dibromotetracyclo[5.4.1.0^{1,7}.0^{3,5}]dodec-9-ene (29). A suspension of **28** (6.0 g, 0.041 mol) and potassium *tert*-butoxide (5.52 g, 0.049 mol) in pentane (100 mL) was treated with bromoform (12.5 g, 0.049 mol) in the manner described above. Following a similar workup procedure, the resultant oil was distilled to give recovered starting material (1.25 g) and **29** (5.51 g, 53% based on unrecovered starting material) as a pale yellow oil: bp 112-114 °C (0.1 mm); ^{1}H NMR (δ, $CDCl_3$) 5.60-5.47 (m, 2 H), 2.60-2.37 (m, 4 H), 2.30-1.83 (m, 6 H), 1.20-0.77 (m, 2 H), and 0.67-0.00 (m, 2 H); ν_{max} (film) 3010, 2925, 2870, 2825, 1448, 1428, 1015, 776, 721, and 657 cm^{-1}; *m/e* calcd 315.9463, obsd 315.9469.

Pentacyclo[6.4.1.0^{1,3}.0^{2,8}0^{4,6}]dodec-10-ene (30). To a solution of **29** (2.5 g, 7.9 mmol) in dry ether (50 mL) stirred under argon at 0 °C was added dropwise during 0.5 h a solution of methyllithium in ether (5 mL of 1.75 M, 8.8 mmol). Stirring was continued at 0 °C for 1 h and then at room temperature for 2 h. The progress of reaction was arrested by the addition of water (50 mL) and the aqueous phase was extracted with ether (50 mL). The combined organic layers were washed with saturated sodium chloride solution, dried, and concentrated. Distillation of the residue gave **30** (0.60 g, 48%) as a colorless oil: bp 30-32 °C (0.07 mm); ^{1}H NMR (δ, $CDCl_3$) 5.70-5.50 (m, 2 H), 2.93-2.80 (m, 1 H), 2.57-0.50 (m, 10 H), and 0.30-0.10 (m, 1 H); ν_{max} (film) 3065, 3020, 2890, 1430, 1015, 818, 762, 755, 702, 690, and 648 cm^{-1}; ^{13}C NMR (ppm, $CDCl_3$) 124.67 (d), 124.48 (d), 45.59 (d), 43.99 (s), 29.47 (t), 25.39 (d), 24.86, (t), 18.11 (s), 12.77 (d), 12.04 (t), 6.11 (t), and 6.12 (d); *m/e* calcd 158.1095, obsd 158.1098.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.87; H, 8.92.

Tricyclo[6.4.0.0^{4,6}]dodeca-1(8),2,10-triene (31). A solution of **30** (150 mg) in benzene (20 mL) containing dissolved silver perchlorate (200 mg) was stirred at room temperature under argon for 24 h. The usual workup gave 95 mg (63%) of **31** which was purified for analysis by preparative VPC: ^{1}H NMR (δ, $CDCl_3$) 7.1-6.9 (m, 1 H), 6.35-6.2 (m, 1 H), 6.1-5.25 (br m, 2 H), 3.1-0.5 (series of br m, 10 H).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.67; H, 8.97.

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Twofold Cyclopropylidene C–H Insertion as a Route to Hexacyclic Bis(bicyclo[1.1.0]butanes) and Their Silver(I) Ion Promoted Rearrangement. A Direct Synthesis of Heptalene from Naphthalene[1]

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Abstract: A method for effecting the twofold ring expansion of a bicyclic diene using the technique of double "naked" carbon atom insertion is described. The substrate is first transformed to its bisdibromocyclopropane derivative by reaction with dibromocarbene. Treatment with an excess of alkyllithium reagent induces carbenoid cyclization to a highly strained bis(bicyclo[1.1.0]butane). When suitable conformational constraints are present, this ring-forming reaction can be regiospecific. Isomerism of these polycyclic products with Ag^+ leads to the thermodynamically more stable ring-opened polyolefins. A short, convenient conversion of naphthalene to heptalene illustrates one useful application of the method. A number of relevant mechanistic facets to this chemistry are also discussed.

The development of an efficient method for the regiospecific insertion of a "naked" carbon atom into an organic molecule has commanded attention in recent years because of its latent significance in synthesis. In an early development, allenes such as **2** were shown to be directly available from alkenes in a single operation. Subsequent to initial reaction with methyllithium and carbon tetrabromide which gives a dibromocyclopropane, in situ treatment with a second equivalent of the alkyllithium delivers product[4] (eq 1; the asterisk notation is utilized for the purpose of identifying the locus of the inserted carbon atom). Comparable treatment of 3-norcarene (**3**) has the virtue of leading stereoselectively to **4** which may be cleanly isomerized to either **5** or **6** depending upon conditions (eq 2).[5] In yet another example, the sesquiterpene ishwarane (**8**) has been prepared from octalin **7** (eq 3).[6] In this instance, C–H insertion by the cyclopropylidene intermediate occurs into the more distal angular methyl group.

A regiocontrolled approach to the singlefold ring expansion of bicyclic olefins and dienes was described in the preceding paper.[1] The excellent regiochemistry observed was attributed

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