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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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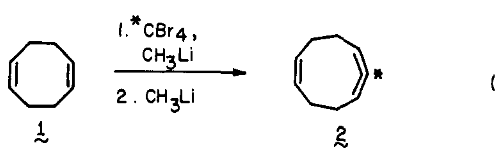

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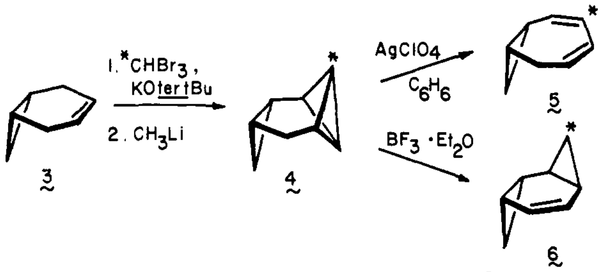

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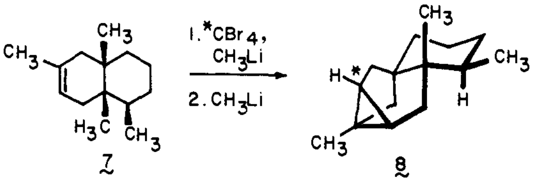

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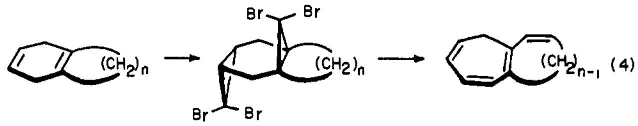
to the very high selectivity of cyclopropylidenes in C$_\alpha$–H insertion reactions. This discrimination appears in turn to be dictated by proximity factors and C$_\alpha$–H bond nucleophilicities.[5,7] In conjunction with studies directed toward the rapid elaboration of medium-ring nonbenzenoid compounds of which heptalene is prototypical, we investigated the possibility of achieving twofold "naked" carbon atom insertions along the lines outlined in eq 4. Although the intended transformations



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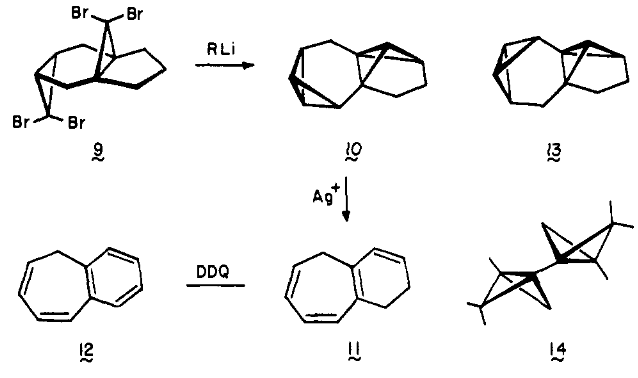
require the intervention of exceedingly strained bis(bicyclo[1.1.0]butanes), we have discovered that such reactive molecules can be produced in good yield and readily handled. Indeed, we have also determined that these interesting compounds are formed regiospecifically when certain structural features are present. Consequently, the overall scheme represents an extremely facile technique for double ring expansion, while simultaneously increasing the number of degrees of unsaturation in the starting diene by two.

Bicyclic Systems. The reaction of tetrabromide **9**, prepared from indan, with ethereal methyllithium at room temperature led to a mixture of the bisbicyclobutane **10** (10%) and an ether insertion product (62%). Although this pair of substances could be easily separated by vacuum distillation, a desire to enhance the yield of **10** prompted examination of the efficacy of *n*-butyllithium in hexane as the cyclization agent. Under these conditions, the level of purified **10** was increased to 31%. In view of the strain energy of a single bicyclo[1.1.0]butane ring (66.5 kcal/mol),[8] we estimate that the destabilization in **10** and related molecules which materializes from this source amounts to 123 kcal/mol. Despite this, we have found it possible to purify **10** on a specially treated all-glass VPC column (0.2% SE-30 on 60/80 mesh glass beads; detector bypass) at 130 °C.

The colorless, oily hydrocarbon was determined to be homogeneous on the basis of its ^{13}C NMR spectrum, which shows only 11 lines. The evidence that the product was indeed **10** and not the isomeric **13** rests chiefly upon Ag$^+$-promoted isomerization to **11**, whose electronic spectrum indicated that all four double bonds were in extended conjugation. Through consideration of the Fieser-Woodward rules, **11** would be expected to exhibit a maximum in the vicinity of 364 nm, if the molecule could become completely planar. In contrast, the cross-con-

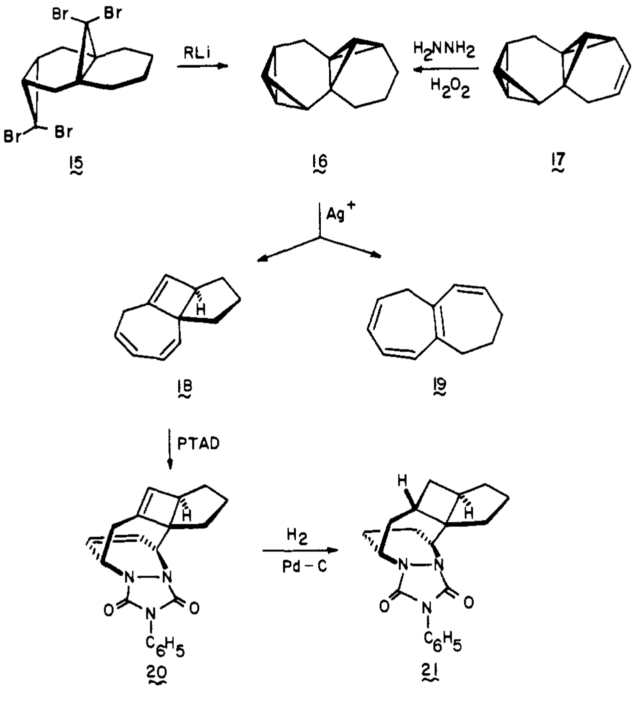


jugated tetraene formally derived from **13** should absorb only below 298 nm. The observed value of 316 nm conforms more closely to that expected for **11**, especially since the seven-membered ring is certainly nonplanar. Additionally, the close correspondence of **10** to two homologous bisbicyclobutanes to be described below, whose structures were established unequivocally, lends further credence to the assignment.

It is noteworthy that the two stereoisomers of **14** are the only molecules of the bisbicyclobutane type to have been previously synthesized successfully (by a different route).[9]

Tetrabromide **15** is so constructed that its twofold carbenoid cyclization cannot result in the formation of a tricyclohexane part structure (as contained, for example, in the right-hand segments of **10** and **13**). Perhaps because of the lessened steric strain, treatment of **15** with methyllithium in ether and ether-pentane solvent systems, or with *n*-butyllithium in pentane, provided bisbicyclobutane **16** in improved and roughly comparable yields (46, 44, and 32%, respectively). Under the first two sets of conditions, a product of insertion into the ethereal solvent was formed simultaneously and isolated in 28 and 31% yields, while in the latter reaction an *n*-butyl exchange product was also obtained (46%).

To establish the regiochemical relationship of the bicyclobutane rings in **16**, recourse was made to the related hydrocarbon **17** whose structure will subsequently be proven in un-



equivocal fashion. For the conversion of **17** to **16**, it was necessary to reduce the double bond without disturbing the bicyclobutane rings. Since acids and transition metals of the type used in catalytic hydrogenation rapidly isomerize such strained

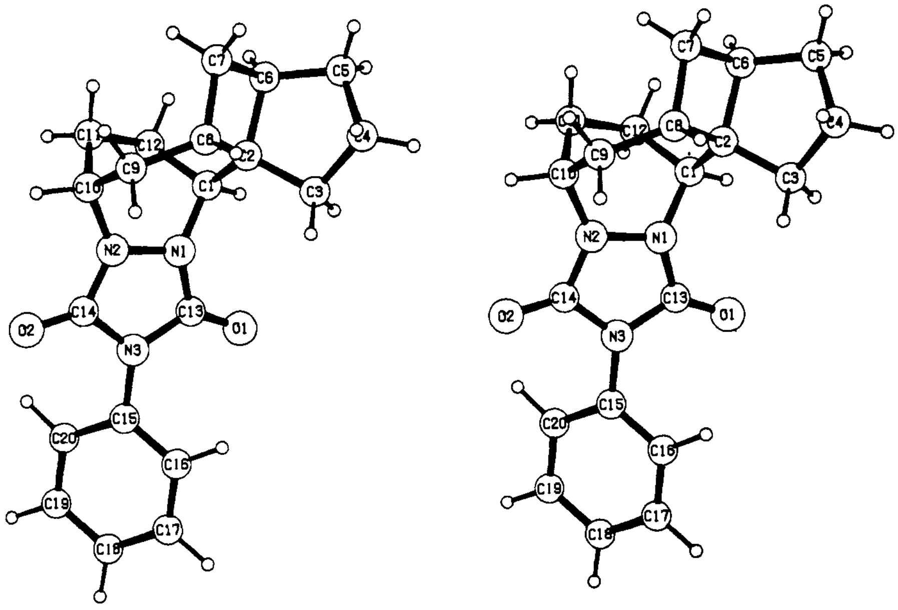


Figure 1. Stereoscopic view of **21** as determined by X-ray analysis.

structures, techniques involving these reagents could not be employed. However, the use of diimide, as generated by the action of hydrogen peroxide on hydrazine,[10] successfully avoided possible rearrangement and gave **16**, as determined by comparison of ^1H and ^{13}C NMR spectra. Thus, the utilization of select chemical agents for performing synthetically useful reactions on sensitive bisbicyclobutanes is not at all precluded.

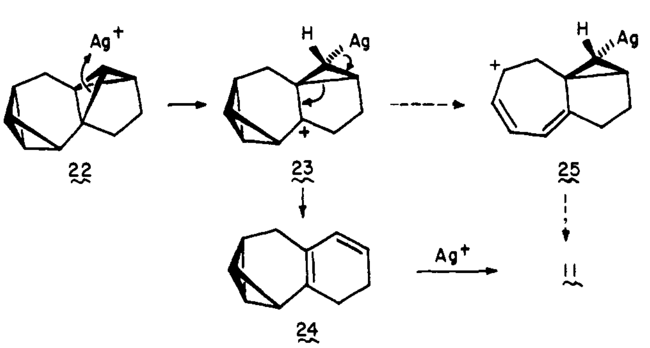
The behavior of **16** upon exposure to silver(I) ion differed markedly from that of related bisbicyclobutanes. Under anhydrous conditions in benzene, no rearrangement at all was observed at room temperature in the presence of silver perchlorate. Isomerization was initiated when the solutions were warmed to ~50 °C. However, instead of simply providing the customary type α rearrangement[11] product **19**, a triene was actually formed as the major product (ratio 1:5.5). This $C_{12}H_{14}$ hydrocarbon exhibits a ^1H NMR spectrum indicative of the presence of five olefinic, three allylic, and six aliphatic protons. Its ^{13}C NMR spectrum indicates the following carbon distribution: one quaternary and five tertiary trigonal centers, in addition to one quaternary, one tertiary, and four secondary tetrahedral atoms. From the ultraviolet maximum (λ_{max} 263 nm in C_2H_5OH), the presence of a homoannular conjugated diene can be inferred. This feature of the molecule was confirmed by Diels-Alder reaction with *N*-phenyltriazolinedione. The 1:1 adduct, which formed rapidly, contained two residual double bonds, as expected, and could be converted back to **18** by suitable hydrolysis-oxidation. Despite its unsaturated nature, this substance failed to react with *N*-bromosuccinimide in refluxing carbon tetrachloride, *m*-chloroperbenzoic acid in dichloromethane, or DDQ in refluxing benzene. One equivalent of bromine was slowly consumed, but a characterizable crystalline product was not obtained. The intense deactivation experienced by a double bond situated in close proximity to a powerful electron-withdrawing urazole ring has been previously commented upon.[12] The inability of this $>C=C<$ linkage to enter into reaction can be understood in these terms. Although the second double bond in **20** may also be subject to similar (although necessarily lessened) untoward inductive effects, its lack of reactivity was thought to be due more to a sterically hindered environment.

With the added benefit of double-resonance ^1H NMR studies on **20**, we were able to reduce the number of structural possibilities to a small number, but did not find it possible to distinguish unequivocally between them. An X-ray crystal structure analysis was accordingly in order, but **20** unfortunately crystallizes in powdery forms unsuited to such purposes. However, its hydrogenation product (**21**) was obtained as high-quality, colorless needles.

The crystals of **21** proved to be monoclinic, space group $A2/a$, with $a = 25.054$ (3) Å, $b = 7.365$ (1) Å, $c = 18.665$ (2) Å, $\beta = 93.00$ (1)°, and $d_{calcd} = 1.303$ g cm^{-3} for $Z = 8$ ($C_{20}H_{23}N_3O_2$, mol wt 337.42). The intensity data were measured on a Hilger-Watts diffractometer (Ni filtered Cu Kα radiation, θ-2θ scans, pulse height discrimination). A crystal measuring approximately 0.10 × 0.10 × 0.5 mm was used for data collection. A total of 2307 reflections were measured for $\theta < 57°$, of which 1813 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[13] and was refined by full-matrix least squares. Five reflections which were strongly affected by extinction were excluded from the final refinement and the final difference map. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.040$ and $wR = 0.043$ for the remaining 1808 observed reflections. The final difference map has no peaks greater than ± 0.2 e A^{-3}.

A stereoscopic drawing of the molecule is given in Figure 1. Tables of the final atomic parameters, bond lengths, bond angles, and selected torsion angles are provided as supplementary material.

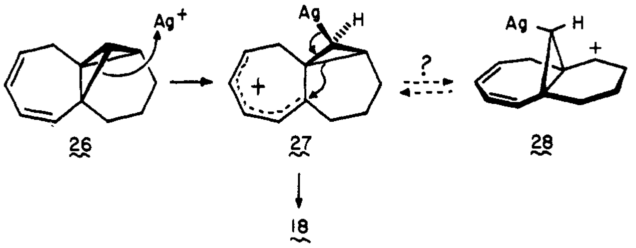
An analysis of the differing response of **10** and **16** to Ag$^+$ catalysis is informative. Although the question of which bicyclobutane entity enters into reaction first has not been probed directly, tricyclo[3.1.0.0^{2,6}]hexane has previously been shown to isomerize more rapidly than tricyclo[4.1.0.0^{2,7}]heptane.[14] On this basis, it is not unrealistic to adopt the working hypothesis that the centrally located bicyclobutane ring in **10** is the site of the initial bimolecular reaction. Edge attack of Ag$^+$ from above the flap as shown in **22**, followed be deargentation, generates the cyclohexadiene **24**. A second type α isomerization within **24**, a reaction course similarly well founded in precedent,[15] would afford **11**. Alternatively, intermediate cation **23** could "unzip" completely to give **25**, a possible direct precursor of **11**. However, this is not the ring-opening mode



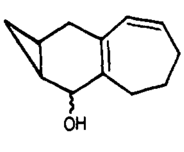
customarily followed by tricyclo[4.1.0.$0^{2,7}$]hept-3-yl cations generated under solvolytic conditions.[16]

Of course, **16** is capable of similar chemistry and presumably undergoes partial conversion to **19** analogously. But the favored transformation involves a mixed type γ-type α bond reorganization to deliver **18.** This dichotomy is perceived to be the result of a heightened rate of isomerization of the peripheral bicyclobutane ring, such that conversion to **27** is kinetically dominant. Contributing in a major way to this phenomenon is the near equalization of steric strain in the two halves of the molecule.

To conform with established concepts,[17] the picture that emerges for the ensuing type γ rearrangement is one that positions the attacking Ag^+ below the plane of the bicyclobutane ring in **26.** Ensuing σ-bond rupture is presumably guided by formation of the delocalized cation **27** whose deargentation can lead directly to **18.** Cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement of **27** to **28** is not only unlikely on thermodynamic grounds, but the newly generated cation would also find it difficult to undergo conversion to type α product (Bredt strain). Therefore, the sequence **26** → **27** → **18** constitutes the most energetically expedient route to a kinetically stable product.



When the silver(I)-catalyzed rearrangement of **16** was carried out under aqueous conditions, **18** and **19** were again formed, but in low (15 and 9%) yields. The major product was an alcohol which conforms structurally to **29** or **30.** On the basis of the mass spectrum, a molecular formula of $C_{12}H_{16}O$ is indicated, in agreement with the monohydration of **16.** The presence of a cyclopropane ring was inferred from a multiplet of area 2 at δ 0.49-0.28, as was a pair of olefinic protons (m, δ 6.12-5.88).



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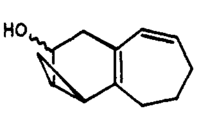

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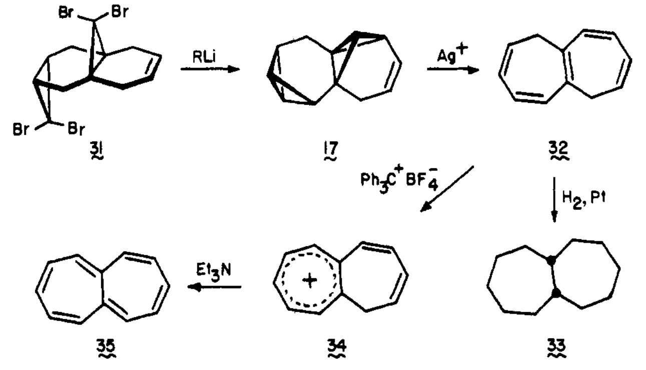
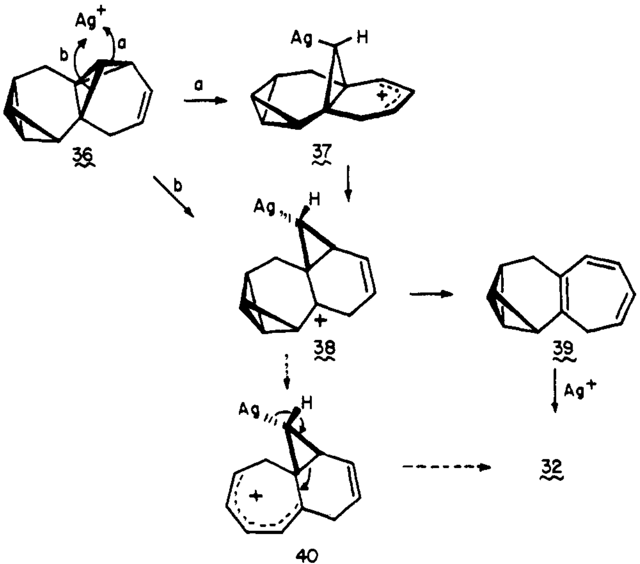
Heptalene Synthesis. Although heptalene (**35**), a theoretically interesting[18] polyolefin with a cyclic 12π-electron network, was first synthesized by Dauben and Bertelli as early as 1961,[19] the hydrocarbon has remained difficultly accessible. The two new syntheses of **35** which have appeared in recent years, although elegant, remain lengthy.[20,21] We now describe an efficient six-step conversion of naphthalene to **35** which is founded upon regiospecific twofold intramolecular cyclopropylidene insertion within **31.**[22]

Treatment of **31**[23] with 2 M ethereal methyllithium proceeded with anticipated regiospecificity to give bisbicyclobutane **17** in remarkably good (59% distilled) yield. Its ^1H NMR spectrum (C_6D_6) contains two series of multiplets at δ 6.03-5.06 (2 H) and 2.46-1.11 (10 H), while its ^{13}C NMR exhibits 12 lines, thereby demonstrating the isomeric homogeneity of this product. The definitive structural assignment to **17** follows from its Ag^+-catalyzed isomerization exclusively to 1,6-dihydroheptalene (**32**). Because **32** belongs to the C_{2h} point group, its ^{13}C NMR should consist of only six lines, as is observed. The alternative 1,10-dihydroheptalene possibility has C_{2v} symmetry and would require a seven-line spectrum. Catalytic hydrogenation of **32** gave the known *cis*-bicyclo[5.5.0]dodecane (**33**).[19] The subsequent conversion of **32** via **34** to **35** was carried out according to Dauben's original procedure.[19]



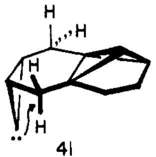
Bicyclobutane **17** is seen to respond to the presence of Ag^+ ions by undergoing double type α rearrangement. Therefore, its chemical behavior conforms to that exhibited by **10** rather than that shown by the more closely allied structural analogue **16.** At the mechanistic level, this experimental result can be attributed to the heightened reactivity[15] of the tricycloheptene part structure in **17** relative to the tricycloheptane moiety. Thus, it may be argued that the isomerization of **17** is initiated by transition metal ion induced ring opening as illustrated in **36** to generate either **37** or **38.** As previously alluded to in the case of **28,** it is unlikely that allylic cation **37** can experience direct deargentation. However, if it be assumed that the operational device of cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement is suited to transform **37** to **38** or that the latter intermediate be formed directly from **17,** then the



ultimate outcome of the reaction must be **32** as previously discussed.

Although the pair of bicyclo[1.1.0]butane rings within **10**, **16**, and **17** is formally conjugated, these molecules exhibit merely typical end absorption in the ultraviolet. It would appear therefore, that electronic interaction between bicyclobutane orbitals can be observed only when the interconnective σ bond is linked to bridgehead carbon atoms.[9]

Origin of the Cyclization Regiospecificity. Of the various lines of mechanistic inquiry opened in the present investigation, that involving the source of the regiospecific twofold cyclopropylidene insertion also deserves comment. No matter which bicyclobutane ring evolves first, a structure substantially more rigid than the starting carbenoid is necessarily formed. The rather pronounced conformational twist which characterizes the resulting tetracyclic intermediates projects the second carbenoid into an environment where it is forcibly held nearest to an axial proton situated most remotely from the existing bicyclobutane ring. Molecular models suggest this compressional effect to be more severe when the first closure has occurred in the central area of the molecule (see **41**) than when peripheral closure has initially taken place as in **42**. In either case, the well-established interdependence of cyclopropylidene reactivity and axial C_α–H bond proximity[1] can be expected to foster kinetically controlled insertion as shown. The outcome is formation of the more distal bisbicyclobutane isomer. Thus, the observed regiospecificity appears to have its origins in the conformational constraints generated by the first-formed bicyclobutane ring.



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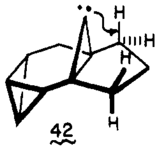
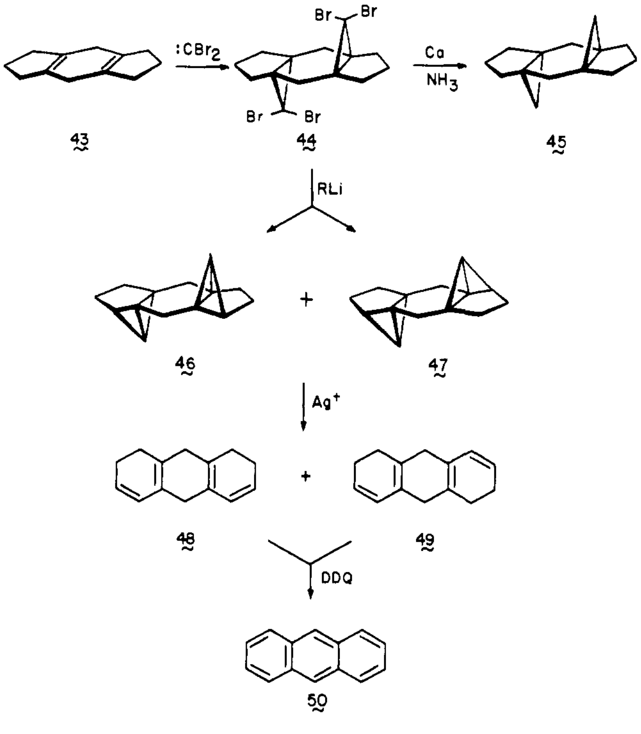
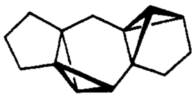


42

Tricyclic Systems. Our attention was next focused on the double ring expansion of representative tricyclic dienes. Addition of dibromocarbene to 4,8-dihydrohydrindacene (**43**)[24] gave in 72% yield the tetrabromide **44** whose stereochemistry was established by dissolving metal reduction to the known hydrocarbon **45**.[24] When exposed to methyllithium or *n*-butyllithium, **44** was converted in 38% yield to a mixture of the bisbicyclobutanes **46** and **47**. The ^{13}C NMR spectrum of this hydrocarbon sample displays 14 lines. Therefore, a mixture of **46** (C_2 symmetry, eight lines) and **47** (C_i symmetry, seven lines) can account for this spectrum only if two peaks are overlapping. On the other hand, **51** and **52** are both of C_1 symmetry. Consequently, regiospecific formation of either of these isomers could concisely account for the 14-line spectrum. Since VPC analysis was not successful on this occasion because of on-column decomposition, the cyclization product mixture was directly subjected to Ag^+-catalyzed isomerization. At this point, two incompletely separable tetraenes (**48** and **49**) were apparent on gas chromatography. Their DDQ oxidation led to a single homogeneous product identified as anthracene (**50**). Therefore, intramolecular cyclopropylidene insertion occurs exclusively into the C_α–H bonds of the cyclopentane rings, in full agreement with the reactivity order established previously.[1] However, the twofold cyclization is no longer regiospecific because of the heightened conformational flexibility of the *s*-hydrindacene system.





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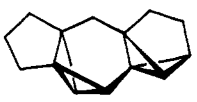
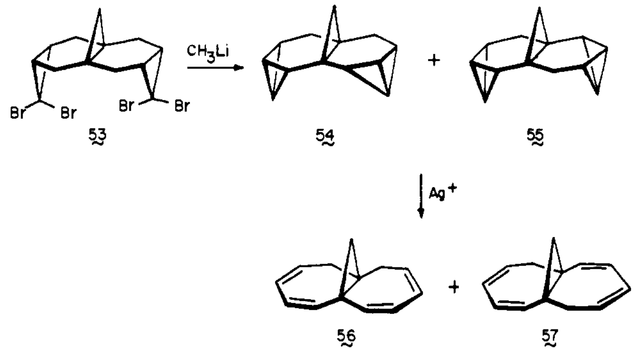


52

In another example, [4.4.1]propella-3,8-diene[25] was converted into the known tetrabromide **53**.[26] Addition of methyllithium to **53** led conveniently to a mixture of **54** and **55** in 52% yield. On the basis of ^1H and ^{13}C NMR analysis, **55** is considered to predominate by a factor of 3:1. The silver ion promoted rearrangement of these bicyclobutanes again required heating (70–75 °C) to produce the mixture of isomeric tetraenes **56** and **57**, known precursors to 1,7-methano[12]-annulene.[26]



Thus, it appears that the exhaustive dibromocyclopropanation of an appropriately constructed cyclic diene, followed by double carbenoid cyclization and transition metal catalyzed isomerization, is a twofold ring expansion sequence of reasonable scope.

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. The Bruker 90 spectrometer was also employed for the recording of ^{13}C spectra. 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.

***anti*-4,4,11,11-Tetrabromotetracyclo[4.3.1.0^{1,7}.0^{3,5}]undecane (9).** This tetrabromide can be isolated from the solids separated prior to recrystallization of 10,10-dibromotricyclo[4.3.1.1^{1,6}]dec-3-ene as prepared from dihydroindan, potassium *tert*-butoxide, and bromoform according to Vogel.[27] Several recrystallizations from chloroform-methanol of the methanol-insoluble solid gave **9** as colorless crystals: mp 169-170.5 °C; ^{1}H NMR (δ, CDCl$_3$) 2.50-1.50 (m); ν_{max} (KBr) 3010, 1445, 1150, and 720 cm^{-1}.

Anal. Calcd for C$_{11}$H$_{12}$Br$_4$: C, 28.48; H, 2.61. Found: C, 28.59; H, 2.68.

Hexahydro-1,3a,7a:4,5,6-dimethenoindene (10). A. Reaction of 9 with Methyllithium. A stirred solution of tetrabromide **9** (60 g, 130 mmol) in 300 mL of dry ether cooled to −10 °C and maintained under argon was treated dropwise with a 1.84 M solution of ethereal methyllithium (210 mL, 390 mmol). After 12 h, the clear solution was washed with water (twice), dried, concentrated, and distilled through a short Vigreux column (bp 26-29 °C, 0.03 mm) to yield the colorless bisbicyclobutane **10** (1.84 g, 10%). Preparative VPC purification on a specially treated 10 ft × 0.25 in. glass SE-30 column at 130 °C yielded an analytical sample: ^{1}H NMR (δ, C$_6$D$_6$) 2.65-1.02 (m); ^{13}C NMR (ppm, C$_6$D$_6$) 40.8, 40.4, 39.8, 34.8, 29.3, 27.6, 18.3, 14.3, 12.4, 5.8, and 4.8; *m/e* calcd 144.0939, obsd 144.0944.

Anal. Calcd for C$_{11}$H$_{12}$: C, 91.61; H, 8.39. Found: C, 91.26; H, 8.48.

Continued distillation of the residue (bp 63-66 °C, 0.03 mm) provided a colorless ether insertion product (17.43 g, 62%): ^{1}H NMR (δ, neat) 3.75-3.20 (m, 2 H), 2.89 (quintet, J = 7 Hz, 1 H), and 2.60-0.20 (m, 19 H); ν_{max} (film) 3030, 1445, 1370, and 1105 cm^{-1}; *m/e* calcd 218.1671, obsd 218.1676.

B. Reaction of 9 with *n*-Butyllithium. A hexane solution 0.68 M in *n*-butyllithium (1.5 mL, 1.03 mmol) was added dropwise to a stirred suspension of tetrabromide **9** (200 mg, 0.431 mmol) in 10 mL of hexane at 25 °C. After 18 h, the mixture was washed with water, dried, and concentrated. Molecular distillation of the residue yielded hydrocarbon **10** (19 mg, 31%).

1,2-Dihydro-5*H*-benzocycloheptatriene (11). A solution of bisbicyclobutane **10** (1.2 g, 8.3 mmol) in 10 mL of benzene was stirred during the addition of 10 drops of 0.2 M silver perchlorate-benzene solution. After being stirred overnight, the resulting solution was washed with ammonia and brine, dried, and concentrated under reduced pressure to yield the tetraene **11** (0.95 g, 79%). Preparative VPC purification (5 ft × 0.25 in. 10% Carbowax 20M, 150 °C) yielded the analytical sample: ^{1}H NMR (δ, C$_6$D$_6$) 6.41 (d of d, J = 3.5 and 0.9 Hz, 1 H), 6.18-5.18 (m, 5 H), 2.35 (d, J = 6.8 Hz, 2 H), and 2.26-1.85 (m, 4 H); λ_{max} (EtOH) 316 nm (ε 7040) and 242 (6100); *m/e* calcd 144.0939, obsd 144.0942.

Anal. Calcd for C$_{11}$H$_{12}$: C, 91.61; H, 8.39. Found: C, 91.55; H, 8.43.

Benzocycloheptatriene (12). Bisbicyclobutane **10** (2 drops) was filtered through a 0.5-g plug of silver nitrate impregnated basic alumina (10%). Elution was made with 1 mL of benzene-d_6 and the eluate was stirred overnight at the reflux temperature with a spatula full of DDQ. Oxidizing agent residues were removed by filtration through a plug of alumina, and the filtrate was concentrated at atmospheric pressure with a Snyder column. Preparative VPC purification (10 ft × 0.25 in. glass SE-30, 135 °C) yielded benzocycloheptatriene (**12**): ν_{max} (film) 3020, 1490, and 1455 cm^{-1}; ^{1}H NMR (δ, CDCl$_3$-CCl$_4$) 7.31-6.99 (m, 4 H), 6.60-5.66 (m, 4 H), and 3.02 (d, J = 6.5 Hz, 2 H). This spectrum completely matched that of authentic material.[28]

***anti*-4,4,12,12-Tetrabromotetracyclo[5.4.1.0^{1,7}.0^{3,5}]dodecane (15).** As in the case of **9**, tetrabromide **15** was isolated from the residues obtained after methanol extraction of 11,11-dibromotricyclo[4.4.1.0^{1,6}]undec-3-ene from the reaction of dihydrotetralin with dibromocarbene. Recrystallization of the sludge from chloroform-methanol furnished pure tetrabromide: mp 157-159 °C (lit.[23] mp 158-158.5 °C); ν_{max} (KBr) 3025, 1430, 1112, and 735 cm^{-1}.

Octahydro-1,2,3:4a,5,8a-dimethenonaphthalene (16). A. Reaction of 15 with Methyllithium in Ether. Freshly recrystallized tetrabromide **15** (50 g, 105 mmol) was stirred in 1 L of dry ether at −20 °C under argon during the dropwise addition of a 1.8 M methyllithium solution (175 mL, 314 mmol). The solution was allowed to warm to room temperature with stirring for 18 h, washed with water, dried, and concentrated. Distillation of the residue through a Vigreux column afforded first 7.71 g (46%) of bisbicyclobutane **16**, bp 52-58 °C (0.2 mm), and 6.76 g (28%) of an ether insertion product, bp 102-103 °C (0.2 mm). Preparative VPC purification (0.2% SE-30 on glass at 135 °C) yielded analytical samples. Bisbicyclobutane **16**: ^{1}H NMR (δ, C$_6$D$_6$) 2.52-2.43 (m, 3 H), and 2.27-1.08 (m, 11 H); ^{13}C NMR (ppm, C$_6$D$_6$) 46.3, 44.5, 40.6, 40.2, 23.6, 22.2, 20.4, 20.2, 15.4, 14.9, 5.0, and 4.3.

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.08; H, 8.92. Found: C, 91.09; H, 9.11.

Ether insertion product: ^{1}H NMR (δ, neat) 3.76-3.20 (m, 2 H), 2.88 (quintet, J = 6 Hz, 1 H), and 2.64-0.32 (m, 21 H); *m/e* calcd 232.1827, obsd 232.1832.

B. Reaction of 15 with Methyllithium in Ether-Pentane. A 2 M methyllithium solution (291 mL, 580 mmol) was added dropwise to a stirred suspension of tetrabromide **15** (92.7 g, 194 mmol) in 1.2 L of 2:1 ether-pentane under argon at 10-15 °C. After the mixture was allowed to warm with stirring for 4 h, it was washed with water and alkaline brine, dried, concentrated, and distilled at 43-47 °C (0.2 mm) to yield the bisbicyclobutane **16** (13.6 g, 44%), and at 80 °C (0.1 mm) to give the ether insertion product (14.3 g, 31%).

C. Reaction of 15 with *n*-Butyllithium in Pentane. A stirred suspension of tetrabromide **15** (28.33 g, 59 mmol) in 250 mL of pentane was treated dropwise with 1.2 M *n*-butyllithium (156 mL, 1.87 mol) at 15 °C. After the mixture was allowed to warm with stirring for 48 h, it was washed with water, dried, concentrated, and distilled to yield bisbicyclobutane **16** (3.03 g, 32%) and material boiling at 120 °C (0.1 mm) presumed to be the mono-*n*-butyl exchange product (7.96 g, 46%).

D. Reaction of 15 with *tert*-Butyllithium. A stirred suspension of tetrabromide **15** (20.5 g, 43 mmol) in 100 mL of pentane was treated dropwise with 1.9 M *tert*-butyllithium at 15 °C during 40 min. After the mixture was allowed to warm with stirring for 12 h, it was washed with water and alkaline brine, dried, concentrated, and distilled to yield impure (by ^{1}H NMR) bisbicyclobutane **16** (390 mg, 6%).

E. Diimide Reduction of 17. A cooled (0 °C) solution of unsaturated bisbicyclobutane **17** (200 mg, 1.28 mmol) and 99% hydrazine (900 mg, 28 mmol) in 5 mL of 95% ethanol was treated dropwise (over 15 min) with 1.3 mL of 30% hydrogen peroxide. Subsequent to warming of the mixture during 4 h, it was treated with pentane, washed with water (until neutral), dried, and distilled (75 °C, 0.5 mm) to yield a 45:17 mixture of saturated and unsaturated bisbicyclobutanes (128 mg, 46% based on unreacted starting material). The ^{1}H and ^{13}C NMR peaks of the reduced hydrocarbon matched those of authentic material.

Aprotic Silver(I)-Promoted Rearrangement of 16. Freshly distilled bisbicyclobutane **16** (1.47 g, 9.3 mmol) and 2 mL of anhydrous 0.1 M silver perchlorate solution were refluxed in 10 mL of dry benzene under argon for 8 h. More silver perchlorate solution (2 mL) was added and heating was continued for 12 h. The cooled solution was washed with alkaline brine, dried, concentrated, and distilled (80 °C, 0.05 mm) to yield an 85:15 ratio of hydrocarbons (780 mg, corresponding to 45% triene **18** and 8% tetraene **19**) by VPC (5 ft × 0.25 in. 10% Carbowax 20M, 159 °C). Preparative VPC purification yielded analytical samples. Triene **18**: ^{1}H NMR (δ, C$_6$D$_6$) 5.83-5.41 (m, 5 H), 2.78-2.66 (br m, 3 H), and 1.86-1.14 (m, 6 H); ^{13}C NMR (ppm, C$_6$D$_6$) 147.6, 137.0, 128.2, 124.6, 124.3, 122.5, 61.6, 48.7, 32.1, 31.6, 26.4, and 24.0; λ_{max} (EtOH) 245 nm (ε 18 100), 253 (19 400), and 263 (13 100); ν_{max} (film) 3010, 1645, 1605, 1442, 1412, and 768 cm^{-1}.

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.08; H, 8.92. Found: C, 90.93; H, 8.93.

Tetraene **19**: ^{1}H NMR (δ, C$_6$D$_6$) 6.50-5.28 (m, 6 H) and 2.36-1.68 (m, 8 H); ^{13}C NMR (ppm, CDCl$_3$) 136.1, 135.5, 134.9, 131.9, 129.0, 125.9, 125.4, 122.1, 35.1, 34.2, 31.3, and 30.9; *m/e* calcd 158.1095, obsd 158.1098.

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.08; H, 8.92. Found: C, 91.13; H, 8.95.

Aqueous Silver(I)-Catalyzed Rearrangement of 16. A solution of bisbicyclobutane **16** (2 g, 12.7 mmol) in 10 mL of tetrahydrofuran was added during 0.5 h to a stirred solution of 0.5 g silver nitrate in 40 mL of tetrahydrofuran-water (3:1) at 50 °C. The mixture was cooled, treated with pentane, and washed with alkaline brine. The organic phase was dried, concentrated, and flash distilled to provide a colorless liquid containing some white solid material. The liquid was dissolved in cold pentane and decanted from the solid. Concentration of the pentane solution provided a mixture (630 mg) containing hydrocarbons **19** and **18** as well as a third compound in a 19:29:40 ratio (corresponding to 15% of triene **18** and 9% of tetraene **19**) according to VPC (4 ft × 0.25 in. 10% SE-30, 115 °C). Sublimation of the remaining solid at 60-80 °C (0.2 mm) provided alcohol **29** or **30** (480 mg, 2): mp 52-62 °C; ^{1}H NMR (δ, CDCl$_3$) 6.12-5.88 (m, 2 H), 3.48

(br s, 1 H), 2.56 (br s, 1 H), 2.14–1.18 (m, 10 H), and 0.49–0.28 (m, 2 H); $\nu_{\max}$ (KBr) 3390, 3050, 2995, 1660, 1055, and 709 cm^{-1}; *m/e* calcd 174.1045, obsd 174.1050.

Diels–Alder Addition of *N*-Phenyltriazolinedione to 18. Freshly purified triene **18** (100 mg, 0.633 mmol) was stirred in 5 mL of ethyl acetate under argon during the addition (in several portions) of freshly sublimed *N*-phenyltriazolinedione (144 mg, 0.633 mmol). The initial red solution turned milky pink in 15 min, whereupon methanol (1 mL) was added. After 12 h, the mixture was evaporated to dryness and the residue was recrystallized in several crops of ethyl acetate to yield the colorless adduct **20** (132 mg, 63%): mp 208–209.5 °C; ^{1}H NMR (δ, CDCl$_3$) 7.60–7.26 (m, 5 H), 6.52–6.16 (m, J = 5.8 and 1.5 Hz, 2 H), 5.73 (t, J = 0.8 Hz, 1 H), 5.08–4.96 (m, 1 H), 4.90 (d of d, J = 5.8 and 1.5 Hz, 1 H), 2.74–2.04 (m, 3 H), and 1.80–1.25 (m, 6 H); ^{13}C NMR (ppm, CDCl$_3$) 150.2, 149.2, 144.6, 132.1, 131.6, 130.0, 129.1, 128.8, 127.9, 125.6, 59.6, 55.9, 50.4, 46.0, 34.9, 29.2, 26.6, and 23.8; $\nu_{\max}$ (KBr) 3045, 1760, 1705, and 1412 cm^{-1}; *m/e* calcd 333.1477, obsd 333.1483.

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.88; H, 5.89; N, 12.50.

Regeneration of 18 from 20. A mixture of urazole **20** (101 mg, 0.303 mmol) and 87% potassium hydroxide (200 mg, 3.03 mmol) was refluxed in 20 mL of isopropyl alcohol under argon for 1 h, cooled to 0 °C, acidified with 2.2 mL of degassed 5% hydrochloric acid, neutralized with 0.5 mL of degassed 5% ammonium hydroxide (pH 8), then stirred with manganese dioxide (500 mg, 5.75 mmol) for 12 h. The reaction mixture was filtered and extracted with pentane. The combined organic layers were washed with water (three times) and brine, dried, and concentrated to leave a colorless liquid contaminated with a small amount of white solid (71 mg, 44%). VPC analysis (6 ft × 0.25 in. 5% Carbowax 20M) showed only one volatile component whose infrared spectra matched that of authentic **18**.

Hydrogenation of 20. A solution of urazole **20** (60 mg, 0.18 mmol) in ethyl acetate (10 mL) was treated with 50 mg of 5% Pd/C catalyst and hydrogenated at atmospheric pressure. The uptake of hydrogen corresponded approximately to 2 equiv. The resulting suspension was filtered and the filtrate was evaporated to dryness. The resulting colorless solid was recrystallized from ethanol to give the saturated adduct **21** as colorless needles: mp 137.5–138.5 °C; ^{1}H NMR (δ, CDCl$_3$) 7.57–7.20 (m, 5 H), 4.75–4.50 (m, 1 H), 4.37–4.08 (m, 1 H), and 2.63–1.43 (m, 16 H); $\nu_{\max}$ (KBr) 3065, 2950, 2905, 2880, 1765, 1695, 1597, 1500, 1453, 1415, 1314, 1264, 1120, 751, 686, and 642 cm^{-1}; *m/e* calcd 337.1790, obsd 337.1796.

Anal. Calcd for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87. Found: C, 70.81; H, 6.77.

***anti*-4,4,12,12-Tetrabromotetracyclo[5.4.1.0^{1,7}.0^{3,5}]dodec-9-ene (31).** Following a modification of Vogel's procedure,[23b] tetrahydronaphthalene was treated with bromoform and potassium *tert*-butoxide. Digestion of the resulting solid with chloroform left 0.8% of tris adduct, mp 276–282 °C dec. Evaporation of the chloroform extracts and recrystallization of the residue from chloroform furnished 38% of bis adduct **31**: mp 165–167 °C; ^{1}H NMR (δ, CDCl$_3$) 5.35 (br s, 2 H), 2.39 (br s, 4 H), 2.05 (br s, 2 H), and 1.85 (m, 4 H); $\nu_{\max}$ (KBr) 3035, 2925, 2885, 1298, 1122, 917, 793, 725, and 651 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}Br_4$: C, 30.29; H, 2.54. Found: C, 30.72; H, 2.61.

1,2,3,4,5,8-Hexahydro-1,2,3:4a,5,8a-dimethenonaphthalene (17). A. Reaction of 31 with Methyllithium. Tetrabromide **31** (5.0 g, 10.5 mmol) was stirred as a suspension in anhydrous ether at 0 °C under nitrogen while 2 M methyllithium solution (12 mL, 24 mmol) was added during 30 min. The resulting mixture was allowed to warm with stirring during 3 h, washed with water and brine, dried, and concentrated. Distillation of the residue at 80–100 °C (0.3 mm) provided colorless bisbicyclobutane **17** (960 mg, 59%). An analytically pure sample of this material was unavailable owing to its instability to VPC conditions: ^{1}H NMR (δ, C$_6$D$_6$) 6.03–5.06 (m, 2 H) and 2.46–1.11 (m, 10 H); ^{13}C NMR (ppm, C$_6$D$_6$) 128.9, 121.7, 46.4, 41.1, 40.7, 35.5, 26.6, 19.3, 13.6, 13.1, 5.0, and 4.4; $\nu_{\max}$ (film) 3030, 2990, 1643, 1430, 1135, and 720 cm^{-1}; *m/e* calcd 156.0939, obsd 156.0941.

B. Reaction of 31 with *n*-Butyllithium. Dropwise addition of a 1.6 M *n*-butyllithium solution (87 mL, 140 mmol) to a stirred suspension of tetrabromide **31** (30 g, 63 mmol) in 300 mL of pentane at 15 °C under argon took 2 h. The mixture was allowed to warm with stirring during 1 h, washed with water (twice) and brine, dried, and concentrated. Distillation through a Vigreux column (65–80 °C, 0.7 mm) provided colorless bisbicyclobutane **17** (1.1 g, 11%).

1,6-Dihydroheptalene (32). Unsaturated bisbicyclobutane **17** (960 mg, 6.15 mmol) was stirred in benzene at 25 °C with 5 mL of 0.2 M silver perchlorate solution for 1 h and then washed with brine. Concentration of the dried organic phase and chromatography of the residue on alumina with hexane elution provided pale yellow 1,6-dihydroheptalene **32** (490 mg, 51%): ^{1}H NMR (δ, CDCl$_3$) 6.60 (d, J = 2.8 Hz, 2 H), 6.05 (d of t, J = 9 and 2.8 Hz, 2 H), 5.50 (t, J = 7 Hz, 2 H), 5.29 (d, J = 7 Hz, 2 H), and 2.46 (d, J = 7 Hz, 4 H); $\nu_{\max}$ (film) 3025, 1613, and 1428 cm^{-1}; ^{13}C NMR (ppm, CDCl$_3$) 132.8, 131.0, 125.6, 123.6, 123.0, and 33.6.

***cis*-Bicyclo[5.5.0]dodecane (33).** Dihydroheptalene **32** (100 mg, 0.64 mmol) in 5 mL of ethanol was hydrogenated over 5 mg of platinum oxide at 52 psig in a Paar apparatus for 8 h. After the catalyst was removed by filtration, concentration under reduced pressure provided the bicyclic hydrocarbon previously prepared by Dauben[19] (82 mg, 74% yield). This material was determined to be 96% pure by VPC (5 ft × 0.25 in. 10% Carbowax 20M, 160 °C). Purification was effected by preparative VPC: ^{1}H NMR (δ, CDCl$_3$) 2.0–1.15 (br m); ^{13}C NMR (ppm, CDCl$_3$) 42.2, 34.1, 30.9, and 27.7; $\nu_{\max}$ (film) 2915, 2852, 1455, and 1443 cm^{-1}; *m/e* calcd 166.1721, obsd 166.1724.

Heptalene (35). 1,6-Dihydroheptalene (**32**) was freshly chromatographed on alumina, eluting with pentane. The pentane was removed and the dihydroheptalene was placed under reduced pressure (0.1 mm) for 10 min. A solution of this material (800 mg, 5.13 mmol) in methylene chloride (100 mL, dried and distilled from calcium hydride) was covered with argon and transferred to a drybox. Trityl tetrafluoroborate (1.69 g, 5.13 mmol) was added in small portions and the flask swirled intermittently. The solution quickly took on the red color of hydroheptalenium tetrafluoroborate. After all the trityl salt had been added the flask was left to stand for 30 min prior to evaporation to dryness on a rotary evaporator. The resulting semisolid was covered with 20 mL of dry ether and mixed with a dry glass rod to produce a greenish-yellow solid. The ethereal solution was decanted and the washing procedure twice repeated. The flask was again flushed with argon and the yellow solid was dissolved in dry chloroform (distilled from calcium hydride). The solution was placed under a positive pressure of argon while being cooled to −78 °C. Gaseous trimethylamine was passed through a Drierite tube and then condensed (dry ice–isopropyl alcohol condenser). When 10 mL had condensed, this was quickly added to the hydroheptalenium salt solution which was again placed under argon. The initial brown color of the salt solution immediately dissipated. The reaction mixture was allowed to come to room temperature and the mahogany color of heptalene developed, together with a suspension of trimethylammonium fluoroborate. After standing for 1 h, the reaction mixture was filtered through a medium porosity sinter, all the time maintaining an argon atmosphere by alternating between evacuation of the system and argon pressure. The heptalene solution thus produced was at all times maintained under argon. Evaporative distillation of solvent left a reddish-brown liquid (ca. 45% yield) which exhibited variable-temperature ^{1}H and ^{13}C NMR spectra identical with those reported earlier: (δ, THF-d_8, −80 °C) 5.5–6.0 (m, 6 H) and 5.0 (d, J = 10 Hz, 4 H). No extraneous signals were observed subsequent to complete removal of the tetrahydrofuran.

4,8-Dihydrohydrindacene (43). *s*-Hydrindacene (9.4 g, 59 mmol) and *tert*-butyl alcohol (8.9 g, 120 mmol) in 40 mL of ether were added to sodium (5 g, 220 mg-atoms) dissolved in 125 mL of refluxing liquid ammonia during 1.5 h. After 5 h, the progress of reaction was arrested by dropwise addition of saturated aqueous ammonium chloride solution. The ammonia was allowed to evaporate. Methanol was added and the organic phase was washed with water and brine, dried, and evaporated to give **43** (9.4 g, 99%), greater than 93% pure by ^{1}H NMR. This material was used without further purification.

9,9,10,10-Tetrabromo-*anti*-dimethanoperhydro-*s*-hydrindacene (44). A solution of bromoform (7 g, 27 mmol) in 25 mL of pentane was added dropwise with stirring to a slurry of **43** (2.0 g, 12.5 mmol) and potassium *tert*-butoxide (2.8 g, 25 mmol) in 75 mL of pentane at 0 °C under argon. After 12 h at 25 °C, 100 mL of water was added and the off-white crystals (4.55 g, 72%) were separated by filtration. Recrystallization from chloroform and from chloroform–methanol provided an analytical sample of **44**: mp 259–263 °C dec; ^{1}H NMR (δ, CDBr$_3$) 2.25–2.09 (m, 12 H) and 1.78–1.41 (m, 4 H); ^{13}C NMR (ppm, CDCl$_3$) 52.6, 39.2, 39.0, 31.1, and 26.1; $\nu_{\max}$ (KBr) 1441, 1160, 961, and 794 cm^{-1}; *m/e* calcd 499.7987, obsd 499.7996.

Anal. Calcd for $C_{14}H_{16}Br_4$: C, 33.37; H, 3.20. Found: C, 33.34; H, 3.22.

***anti*-Dimethanoperhydro-*s*-hydrindacene (45).** A solution of tetrabromide **44** (7 g, 13.9 mmol) and *tert*-butyl alcohol (4.2 g, 57 mmol) in 700 mL of tetrahydrofuran was added to 1 L of refluxing liquid ammonia containing excess calcium metal (11.6 g, 290 mg-atoms) during 1.5 h. The progress of reaction was arrested by addition of solid ammonium chloride and the ammonia was allowed to evaporate. Chloroform extracts of the residue were washed with water and brine, concentrated, and distilled at 44-52 °C (0.02 mm) to provide the hydrocarbon (1.77 g, 68%): mp 46-49 °C (lit.[24] mp 49-50 °C); ^{13}C NMR (ppm, CDCl$_3$) 34.5, 32.5, 25.6, 21.5, and 16.9.

Tetrahydro-1*H*,4*H*,5*H*,8*H*-dimetheno-*s*-indacene (47) and Tetrahydro-1*H*,4*H*,5*H*,8*H*-dimetheno-*s*-indacene (46). A. Reaction of 44 with Methyllithium. Powdered tetrabromide **44** (5.03 g, 9.98 mmol) was dried at 0.1 mm in a Schlenk flask and then stirred in 30 mL of ether-pentane (1:1) under argon during the dropwise addition of 2 M methyllithium (15 mL, 30 mmol) at 15 °C. After 4 h, the resulting mixture was washed with water (twice) and alkaline brine, dried, concentrated, and distilled (85 °C, 0.1 mm) to yield 1.32 g of colorless liquid. VPC purification (10 ft × 0.25 in., glass, 0.2% SE-30, 145 °C) afforded an analytical sample of **46/47** (total of 0.70 g, 38%): ^{1}H NMR (δ, C_6D_6) 2.63-2.47 (m, 2 H), 2.06-1.90 (m, 4 H), and 1.49-1.19 (m, 10 H); ^{13}C NMR (ppm, C_6D_6) 44.7, 44.2, 35.7, 31.7, 31.5, 28.4, 27.7, 22.9, 19.2, 16.8, 15.3, 14.4, 11.8, and 11.4; ν_{max} (neat) 3038, 1465, 1445, and 780 cm^{-1}; *m/e* calcd 184.1252, obsd 184.1257.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.22; H, 8.74.

B. Reaction of 44 with *n*-Butyllithium. A 0.68 M *n*-butyllithium solution (10.6 mL, 7.2 mmol) was added over 10 min to a stirred slurry of tetrabromide **44** (1.5 g, 2.98 mmol) in 20 mL of pentane under argon at 25 °C. After 2 h, the mixture was washed with water, dried, concentrated, and distilled to yield the bisbicyclobutanes **46/47** (209 mg, 38%), bp 75 °C (0.01 mm), and an *n*-butyl substitution product (273 mg, 29%): bp 85-90 °C (0.01 mm); ^{1}H NMR (δ, CDCl$_3$) 2.72-0.65 (m); ν_{max} (film) 3020, 1442, 1060, and 815 cm^{-1}; *m/e* calcd 320.1140, obsd 320.1147.

Hexahydroanthracenes 48 and 49. A solution of bisbicyclobutanes **46/47** (200 mg, 1.09 mmol) in 3 mL of dry benzene was degassed and added to 200 mg of dried silver perchlorate dissolved in 30 mL of degassed benzene under argon. After 19 h at 25 °C, the milky white suspension was washed with alkaline brine (twice), concentrated, and distilled (110-115 °C, 0.1 mm) to yield the low-melting (ca. 60 °C) tetraenes **48/49** (151 mg, 75%). VPC analysis (3 ft × 0.25 in., 5% SE-30, 202 °C) indicated 86% purity without separating the two olefins and yielded an analytical sample: ^{1}H NMR (δ, C_6D_6) 5.68 (br s, 4 H) and 2.68-1.70 (br m, 12 H).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.04; H, 8.70.

Oxidation of 48/49 to Anthracene (50). A mixture of the isomeric hexahydroanthracenes **48** and **49** (55 mg, 0.30 mmol) and DDQ (360 mg, 1.6 mmol) was stirred in 5 mL of benzene for 3 h at 25 °C. The resulting orange slurry was chromatographed on alumina with benzene elution. Anthracene (21 mg, 39%), mp 205-210 °C, was isolated and identified by comparison of its ^{1}H NMR spectrum with that of authentic anthracene.

1,1,4,4-Tetrabromooctahydro-1*H*,3*H*-2aα,5aα-methanodicyclopropa[βb,βg]naphthalene (53). Bromoform (38 g, 150 mmol) was added over the course of 3 h to a stirred slurry of [4.4.1]propella-3,8-diene (7.91 g, 54 mmol) and potassium *tert*-butoxide (16 g, 140 mmol) in 150 mL of dry pentane at 0 °C under argon. After 12 h, water was added and the solids were separated by filtration. The precipitate was washed with water and pentane and then recrystallized from chloroform-ethanol in several crops to yield white crystals of **53** (11.5 g, 44%), mp 175-177 °C (lit.[26] mp 169-170 °C).

Octahydro-4a,8a-methano-1,2,3:5,6,7-dimethenonaphthalene (55) and Octahydro-4a,8a-methano-1,2,3;6,7,8-dimethenonaphthalene (54). Pulverized tetrabromide **53** (5.0 g, 10.2 mmol) was dried at 0.1 mm in a Schlenk flask overnight, then stirred as a suspension in 30 mL of ether-pentane (1:1) during the addition of a 2 M methyllithium solution (15.3 mL, 31 mmol) at 15 °C during 15 min. The mixture was allowed to warm with stirring for 4 h, washed with water (twice) and alkaline brine, dried, concentrated, and distilled (80 °C, 0.1 mm) to yield a yellow mixture of two isomers (0.88 g, 52%). Analysis by VPC (10 ft × 0.25 in., glass, 0.2% SE-30, 145 °C) showed primarily two incompletely separated isomers to be present with several other very minor components. Preparative VPC yielded an analytical sample of the **54/55** mixture, which appeared by ^{1}H NMR to be present in a 73:27 ratio: ^{1}H NMR (δ, C_6D_6) 2.50-1.77 (m, 4 H), 1.66 (s, 2 H), 1.64 (s, 2 H), 1.50-1.17 (br m, 4 H), 0.62 (s, 0.73 H), and 0.60 (s, 0.27 H); ν_{max} (film) 3095, 3060, 1422, 1130, and 715 cm^{-1}; *m/e* calcd 170.1090, obsd 170.1095.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.63; H, 8.33.

1*H*,6*H*-5a,10a-Methanoheptalene (57) and 1*H*,10*H*-5a,10a-Methanoheptalene (56). A solution of bisbicyclobutanes **54/55** (440 mg, 2.59 mmol) in 4 mL of benzene was degassed and added dropwise under argon to a stirred solution of dried silver perchlorate (300 mg) in 15 mL of benzene. After being heated with stirring at 70-75 °C for 45 min, the milky yellow mixture was washed twice with alkaline brine, dried, concentrated, and distilled (95-100 °C, 0.1 mm) to provide a yellow oil (220 mg, 50%). Analysis by VPC (3 ft × 0.25 in., SE-30, 118 °C) showed two major components to be present and provided an analytical sample: ^{1}H NMR (δ, C_6D_6) 6.17-5.45 (m, 8 H), 2.65-1.52 (m, 4 H), and 0.62 (s, 2 H).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.54; H, 8.29.

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Supplementary Material Available: The final atomic and anisotropic thermal parameters, bond lengths, bond angles, and selected torsion angles for **21** (Tables I-V, respectively) (3 pages). Ordering information is given on any current masthead page.

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Kinetics of Dissociation of Potassium and Thallium Cryptates

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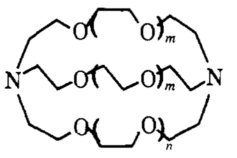
Abstract: The kinetics of dissociation of thallium cryptates $(222\text{Tl})^+$ and $(221\text{Tl})^+$ was studied in water and in methanol-water (90:10) over the range of temperatures 5-35 °C. The kinetic behaviors of $(222\text{Tl})^+$ and $(222\text{K})^+$ in water were compared. For the *direct dissociation* process the kinetic results have shown a similar behavior of $(222\text{K})^+$ and $(222\text{Tl})^+$ in water. A less solvating medium (methanol-water) than water leads to slower dissociation rates of the thallium cryptates studied. The *acid-catalyzed dissociation* path differentiates significantly, in terms of rate constants and activation parameters, the behavior of $(222\text{K})^+$ and $(222\text{Tl})^+$ in acidic aqueous medium.

Introduction

The macrocyclic diamines or "cryptands" synthesized by Lehn et al.[1] are now well known for their ability to form stable complexes with alkali metal ions.[2-6]



(2,1,1) $m = 0; n = 1$
(2,2,1) $m = 1; n = 0$
(2,2,2) $m = n = 1$

Dynamic aspects of these new complexes were first studied by NMR measurements[7-9] and by relaxation methods.[10,11] Flow methods were used by Wilkins et al.[12,13] for the kinetic study of the dissociation of several calcium cryptates in water and by Schneider et al.[14,15] for the study of the acid-catalyzed dissociation and formation rates of some alkali earth and alkali metal cryptates.

In this paper, we report on the influence of the solvent and of the temperature on the kinetics of dissociation of potassium and thallium cryptates. The kinetic behavior of Tl^+ and K^+ cryptates will be compared. K^+ is a cation of prime importance in biochemistry, but its spectroscopic properties are very poor. Tl^+ is now used as a physical probe in biological systems: it replaces K^+ and is easily measured by various techniques (NMR, UV, etc.).[5,16]

For the acid dissociation of a metallic cryptate, the overall reaction can be written

$$(\text{CryM})^{n+} + 2\text{H}^+ \rightarrow \text{M}^{n+} + (\text{CryH}_2)^{2+} \quad (1)$$

with $(\text{CryM})^{n+}$ = metallic cryptate and $(\text{CryH}_2)^{2+}$ = protonated cryptand. We found the same rate law as that observed by Schneider et al.:[14]

$$v = \{k_\text{D} + k_\text{H}[\text{H}^+]\}[(\text{CryM})^{n+}] \quad (2)$$

with k_D = rate constant for the direct dissociation and k_H = rate constant for the acid-catalyzed dissociation of the cryptate.

Experimental Section

Kinetics Procedure. The rates of reaction 1 for potassium and thallium cryptates were measured with a Durrum-Gibson stopped-flow spectrophotometer. The kinetic data were recorded by a transient recorder Datalab and treated on-line with a desk computer Olivetti P652.

Earlier we studied the dissociation kinetics of the potassium cryptate $(222\text{K})^+$ in water and in acidic medium.[17] At 440 nm, with a pH indicator (2,6-dinitrophenol), the variations of the pH vs. time were obtained for reaction 1.

For the thallium cryptates, the experimental conditions were much easier: the dissociation of the complexes was directly observed with the stopped-flow spectrophotometer at 253 nm for $(222\text{Tl})^+$, at 246 nm for $(221\text{Tl})^+$, and at 250 nm for $(211\text{Tl})^+$. Preliminary spectra were measured on a spectrophotometer Cary 17.

The experimental conditions chosen for the kinetic study of the cryptate $(222\text{K})^+$ were already described.[17]

For the kinetic study of the dissociation of the thallium cryptates considered, a solution of acid in excess (HClO_4) was mixed with a solution containing tetramethylammonium hydroxide (10^{-2} mol L^{-1}), the cryptand ($\simeq 10^{-4}$ mol l^{-1}), and 10% excess of Tl^+. The experiments were done at various pH values over the range of 2-3. The ionic strength was controlled with tetraethylammonium perchlorate (0.1 mol L^{-1}).

The activation parameters for both dissociation paths were determined from Eyring plots in the range of 5-35 °C (Figure 1).

Materials. The cryptands (222), (221), and (211) were commercial samples (Merck) used without further purification. Tetramethylammonium hydroxide was obtained as 10% aqueous solutions from Merck.

Results and Discussion

A. Direct Dissociation. As shown in Table I, the cryptates $(222\text{K})^+$ and $(222\text{Tl})^+$ have a similar behavior in their direct dissociation in water: the values of the rate constants are equal.

When we compare $(222\text{Tl})^+$ and $(221\text{Tl})^+$ in water, the dissociation rate becomes larger for $(221\text{Tl})^+$; in methanol-water (90:10), the cryptates $(222\text{Tl})^+$ and $(221\text{Tl})^+$ dissociate at the same rate in the limits of the experimental uncertainties (Table I). It is worth noting that, in the cases of $(221\text{K})^+$ [11,18] and $(221\text{Tl})^+$, respectively, compared with $(222\text{K})^+$ and $(222\text{Tl})^+$ in water, the loss of a binding site and a cavity of the ligand smaller than the ionic radius of the cation lead to larger

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