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Synthesis and Chemistry of Cubanes

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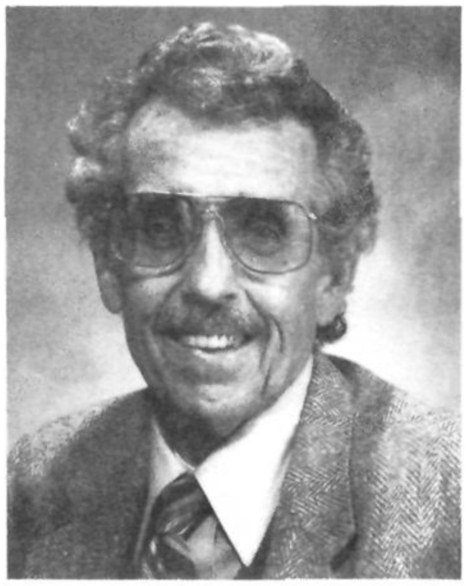
Contents

I. Introduction

Of the five convex Platonic solids,[1] only carbocyclic $(CH)_n$ analogues of the tetrahedron, the cube, and the dodecahedron are potentially accessible to synthetic organic chemists. In fact, examples of all three polycarbocyclic "cage" systems "tetrahedrane" ($n = 4$),[2,3] "cubane" ($n = 8$),[4] and "dodecahedrane" ($n = 20$)[5]] have been synthesized. Of these three systems, pentacyclo-[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane ["cubane" (**1**)] was the first to yield to rational synthesis.[4]

A primary source of aesthetic appeal of cubane lies in its symmetry (O_h point group).[6] In addition, the bond deformations that are required to place eight, formally sp^3-hybridized methine carbon atoms at the vertices of a cube would reasonably be expected to introduce considerable strain into the cubane molecule. This expectation is borne out by experiment: the standard heat of formation of cubane is 144.5 ± 1.3 kcal/mol, which corresponds to a total strain energy of 166 kcal/mol for this molecule.[7,8] Despite the considerable degree of strain in cubane (ca. 14 kcal/mol per carbon–carbon bond),[9] this molecule is extraordinarily stable, surviving essentially unchanged at temperatures up to ca. 200 °C.[8a] Hence, a second source of appeal is the unusual kinetic stability displayed by cubane and by functionalized cubanes. This fact propels such molecules beyond the realm of intellectual curiosities, rendering cubane and its derivatives of potential practical as well as theoretical interest.

In this review, we shall explore the methods by which cubanes are synthesized, thereby documenting some of the ways that synthetic organic chemists are able to take advantage of the unusual kinetic stability of cu-



Professor Gary W. Griffin has been involved in University teaching and research since 1958. He received his B.S. degree from Pomona College in 1953 and his Ph.D. with Professor Reynold C. Fuson in 1956 from the University of Illinois. After 2 years with Humble Oil and Refining Co., Baytown, TX, he was appointed Instructor at Yale University. In 1965 he moved to Tulane University as Associate Professor and concurrently became Visiting Associate Professor at the University of New Orleans. Presently he is Boyd Professor at that institution. Boyd Professor Griffin's group is engaged in a spectrum of synthetic, mechanistic, and bioorganic research projects. Several members of a novel class of hydrocarbons, the radialenes, including trimethylenecyclopropane and tetramethylenecyclobutane, were first synthesized in this group. Dr. Griffin participated in the renaissance that occurred in photochemistry in the 1950s and is coinventor of the widely used Rayonet photoreactor and pressure vessel. Over the past 25 years he and his group have discovered a number of photoinduced reactions, particularly of small rings. In addition, his interests include generation and reactions of carbenes, singlet oxygen, arene oxides, and carbonyl ylides as well as photoinduced electron-transfer-initiated fragmentation processes and highly strained carbocyclic systems. Dr. Griffin is the author or coauthor of several reviews and chapters for advanced monographs on such topics as singlet oxygen, the formation of carbenes by cycloelimination reactions, and photochemistry of three- and four-membered heterocyclic ring systems. He is also coauthor of a monograph entitled *Metabolic Activation of Polynuclear Aromatic Hydrocarbons*. He was consultant to 3M Corp. for a 20-year period (1962–1982) and presently still consults for several companies and institutions.

Professor Alan P. Marchand's biography appears elsewhere in this issue.

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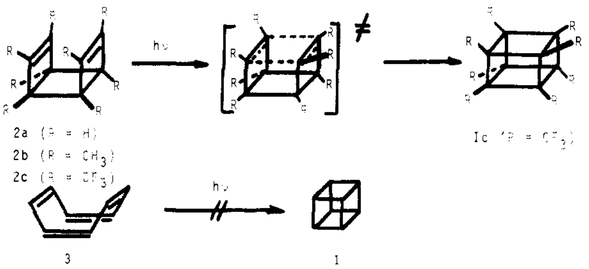
SCHEME 1



bane in the face of what at first glance might appear to be overwhelming thermodynamic odds against its very existence. We shall also examine some reactions of cubanes and thereby explore some of the ways in which the strain energy in cubane manifests itself through enhanced chemical reactivity. Literature coverage extends through October 1988.

II. Synthetic Approaches to Cubane and Substituted Cubanes

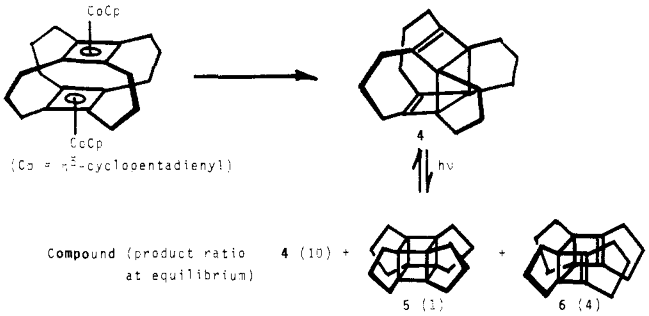
A. Use of Functionalized Noncage Precursors. Cycloaddition Based Approaches

A potentially attractive route for synthesizing cubanes from noncage precursors might involve the use of intramolecular [2 + 2] photocyclizations in appropriately constructed diene (or polyene) precursors. In the case of unsubstituted cubane, this might take the form of (i) photocyclization of the alkene units in *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes (e.g., **2a–c**) or, alternatively, (ii) two [2 + 2] photocyclizations between nonadjacent (nonorthogonal) C=C units in 1,3,5,7-cyclooctatetraene (**3**, Scheme 1). In fact, both types of photocyclization processes have been investigated, with varying degrees of success. Photolysis of **2a**,[10,11] **2b**,[11-13] or **3**[14] fails to afford cubane. One explanation that has been forwarded to account for the failure of, e.g., **2a** to undergo intramolecular [2 + 2] photocyclization is based upon analysis of its photoelectron spectrum. Thus, the geometry of the system is such that a dominant through-bond (rather than through-space) interaction between the C=C centers in **2a** is believed to occur, thereby reversing the relative energies of the in-phase and out-of-phase π combination. This reversal in energy levels renders the suprafacial [2 + 2] photocyclization reaction symmetry-forbidden.[10,15-18] Other arguments have been forwarded that point to the anticipated deleterious effects of strain in the photocyclization product vs the corresponding (less dramatic) effects in the reactant.[11] Also, attention has been focused upon the relatively large nonbonded distance (3.05 Å) that separates the two carbon–carbon double bonds in **2a**.[11]

In contrast to the failure of **2a** and **2b** to undergo the desired photocycloadditions, intramolecular [2 + 2] photocyclizations of appropriately substituted tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes have been carried out successfully to afford the corresponding substituted cubane. Thus, irradiation of either *syn*- (**2c**, Scheme 1) or *anti*-octakis(trifluoromethyl)tricyclo[4.2.0.0^{2,5}]octa-3,7-diene affords octakis(trifluoromethyl)cubane (**1c**).[19]

More recently, a particularly striking example has been reported by Gleiter and Karcher.[20] In the case of

SCHEME 2



4, bridging between the two C=C moieties reduces the nonbonded distance between unsaturation centers in **4** to ca. 2.6 Å (vs 3.05 Å in **2a**).[21] Irradiation of a solution of **4** in degassed pentane at room temperature with a 500-W high-pressure mercury lamp affords an equilibrium mixture of **4**, **5**, and **6** (product ratio 10:1:4, Scheme 2).[20] It was observed that substituted cubane **5** undergoes cycloreversion to **4** either in the presence of trace quantities of acid or thermally (during attempted gas chromatographic purification on a Carbowax OV 101 column at 180 °C).[20,22]

In 1961, Freedman[23] isolated a high-melting solid (mp 430 °C) in 85% yield by thermal decomposition of (4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)dimethyltin bromide [i.e., Ph(Br)C=C(Ph)C(Ph)=C(Ph)Sn(Br)Me$_2$]. On the basis of (i) analysis of the solid-state infrared and Raman spectra of this product and (ii) preliminary results of an X-ray crystallographic study,[24] it was suggested that the product thereby obtained was octaphenylcubane. Other syntheses of this same high-melting solid have been reported [e.g., by reaction of (tetraphenylcyclobutadiene)palladium(II) chloride complex with triphenylphosphine in refluxing benzene].[25,26] Further efforts to characterize this material were reported, and alternative $C_{56}H_{40}$ structures were suggested.[25-27] However, the question of the structure of the "high-melting solid" was resolved by two independent X-ray crystallographic studies, both of which confirmed the fact that this material is octaphenylcyclooctatetraene rather than octaphenylcubane.[28,29]

Direct[30] and sensitized[31] UV irradiation of diphenylacetylene is reported to produce high-melting materials (mp 427–429 °C[30] and mp 425 °C,[31] respectively) in very low yield. On the basis of analysis of infrared[31] and Raman[32] spectral data, it was suggested that this compound, a diphenylacetylene tetramer, is, in fact, octaphenylcubane. No additional evidence to support the suggested octaphenylcubane structure has been reported.

B. Use of Functionalized Cage Precursors. Cycloelimination and Ring Contraction Based Approaches

Cycloelimination reactions on appropriately substituted cage precursors offer a potential method for introducing a new carbon–carbon σ bond into the cage system. In principle, it should be possible in such cases to promote thermal or photochemical extrusion of a neutral molecule (N_2, CO, CO_2, SO_2, etc.) with concomitant formation of a new carbon–carbon σ bond (Scheme 3). Such reactions may proceed as concerted

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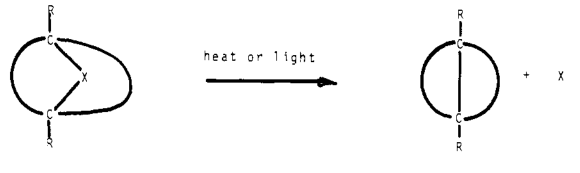

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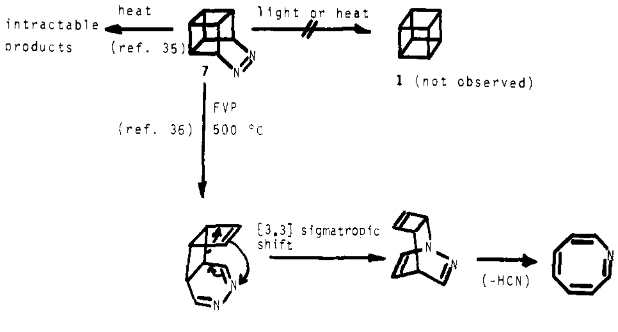

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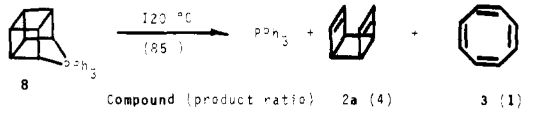

cheletropic processes in accordance with the principles of conservation of orbital symmetry,[33] or they may instead proceed in stepwise fashion via dipolar or diradical intermediates. Indeed, such thermal or photochemical processes are frequently employed for the synthesis of alkenes (wherein loss of a neutral molecule results in the formation of a carbon–carbon double bond). However, relatively few corresponding examples have been reported wherein new carbon–carbon σ bonds have been formed by this route, particularly in cases where the new σ bond would become incorporated into a highly strained polycyclic system.[33]

It was recognized that suitably constructed azoalkanes might serve as precursors for synthesizing new cage molecules.[34] This type of approach has been applied to thermal[35,36] and photochemical[35] decomposition of "diazabasketene" (7). In this example, the expectation that loss of nitrogen might occur with concomitant formation of cubane was not realized (Scheme 4). Another (similarly unsuccessful) example in this regard is provided by the thermal extrusion of triphenylphosphine from compound 8 (Scheme 5).[37]

Ring contractions of suitably substituted homocubanes and bishomocubanes provided the key to the first successful synthesis of the cubane ring skeleton. Thus, Eaton and Cole[4] "elegantly merged known methodology for the construction of this intriguing cage structure"[38] by employing the base-promoted "quasi-Favorskii" or "semibenzilic acid" rearrangement of α-halo ketones in the manner shown in Scheme 6.

It is important to note the use of methanolic HCl as solvent in the intramolecular [2 + 2] photocyclization of **9**. Thus, the species that undergoes photocyclization in this reaction to afford **10** is most likely the bis(hemiketal) of **9** (rather than cage diketone **9** itself). Alternatively, the required photocyclization can be accomplished by irradiation of that monoethylene ketal of **9** in which only the C(10) carbonyl group has been protected.[4] The results of more recent studies by Fuchs and co-workers indicate that the photochemical behavior of halogenated endo cyclopentadienone dimers is quite complex and, accordingly, that irradiation of these diketones is *not* a suitable method for synthesizing halogenated 1,3-bishomocubanediones.[39]

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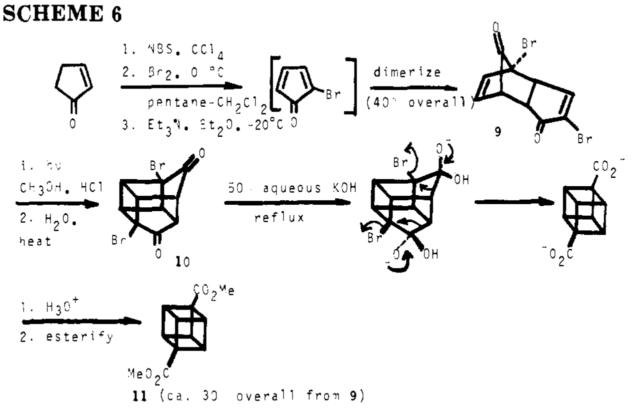
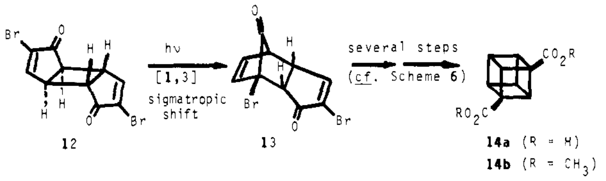
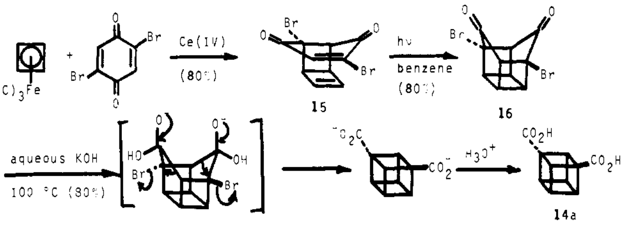


SCHEME 7



SCHEME 8

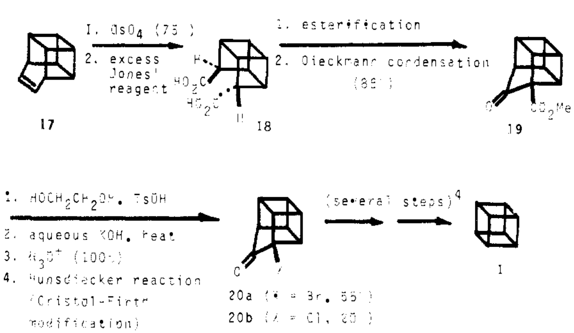


An alternative approach to cubane precursors that involves photochemical rearrangement of substituted *cis,anti,cis*-tricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-diones has been reported.[40] Thus, irradiation of the corresponding 4,9-dibromo compound, **12**, affords compound **13**,[40] a positional isomer of the tricyclic dibromo diketone, **9**, that had been utilized previously by Eaton and Cole[4] in their original synthesis of dimethyl cubane-1,4-dicarboxylate (Scheme 6).[4] It was also shown that **13** could be converted into dimethyl cubane-1,3-dicarboxylate (**14b**) by using the Eaton–Cole[4] procedure (Scheme 7).

Another modification of the original Eaton–Cole entry into the cubane ring system was utilized by Pettit and co-workers in their elegant synthesis of cubane-1,3-dicarboxylic acid (**14a**).[41] Oxidative decomposition of (cyclobutadiene)iron tricarbonyl in the presence of 2,5-dibromobenzoquinone afforded the corresponding endo Diels–Alder cycloadduct (**15**, 80%). Intramolecular [2 + 2] photocyclization of a benzene solution of **15** provided the corresponding dibromo-1,2-bishomocubanedione (**16**) in 80% yield. Finally, treatment of **16** with aqueous potassium hydroxide solution at 100 °C followed by acidification of the cooled reaction mixture afforded **14a** (80% yield, Scheme 8).

Masamune and co-workers[42] reported a formal synthesis of cubane from basketene (**17**). Oxidative cleavage of the carbon–carbon double bond in **17**

SCHEME 9



yielded the corresponding secocubanedicarboxylic acid (18). Esterification of 18 followed by base-promoted Dieckmann condensation of the resulting diester led to the formation of a substituted homocubanone, 19. Compound 19 was converted into the corresponding α-halo ketones, 20a and 20b, by using a standard synthetic sequence (Scheme 9). Since Eaton and Cole[4] had previously synthesized cubanecarboxylic acid by base-promoted semibenzilic acid rearrangement of 20a, the sequence shown in Scheme 9 constitutes a formal cubane synthesis.

Chapman and co-workers[43a] reported having obtained cubane-1,4-dicarboxylic acid in low yield (ca. 9%) via base-promoted double semibenzilic acid rearrangement of Eaton and Cole's[4] dibromobishomocubanedione. A broad range of experimental conditions was examined, but no significant improvement in the yield of cubane-1,4-dicarboxylic acid resulted from these investigations. Subsequently, Luh and Stock[43b] reported that they experienced no difficulty in reproducing the procedure reported originally by Eaton and Cole,[4] and they provided full experimental details of their procedure.

Due in part to the difficulties that some investigators have experienced in their attempts to promote semibenzilic acid rearrangements in strained cage systems, considerable attention has been focused upon the use of this technique as a means to gain synthetic entry into substituted cubanes and other highly strained cage systems.[44,45] Competing Haller–Bauer cleavage[46] is now recognized to be an important side reaction that frequently complicates attempted semibenzilic acid rearrangements in appropriately substituted homocubanones, bishomocubanones, and bishomocubanediones.[43,44] It seems clear that (i) the nature of the substrate and of the leaving group in the substrate and (ii) the choice of reaction conditions are critical to the success of base-promoted semibenzilic acid rearrangements.[43-45] Nevertheless, the "Favorskii-like" contraction of an intermediate bromo ketone remains the singularly successful, tactical entry into the (cubane) system.[8a]

Polyhalogenated 1,3- and 1,4-bishomocubanediones have also been utilized as potential precursors to highly substituted cubanes. Whereas perchloro-1,4-bishomocubanedione (i.e., "kepone") failed to undergo two sequential semibenzilic acid rearrangements when treated with base,[47] the corresponding perbrominated 1,3-bishomocubanedione, 21, proved better behaved in this regard.[48] Thus, of the three possible hexabromocubanedicarboxylic acids (i.e., 22a–c) that might have resulted via double semibenzilic acid rearrangement of 21, in fact, only one product, 22c, was formed.[48] Sub-

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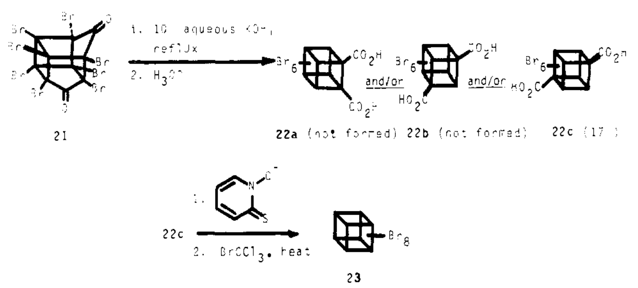
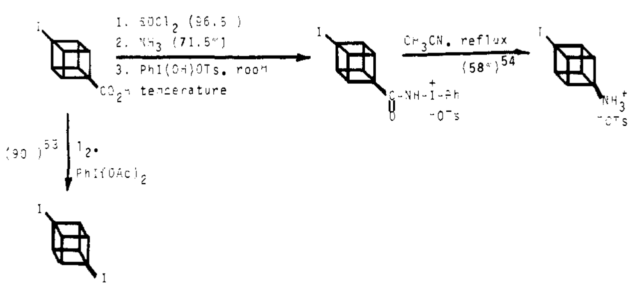
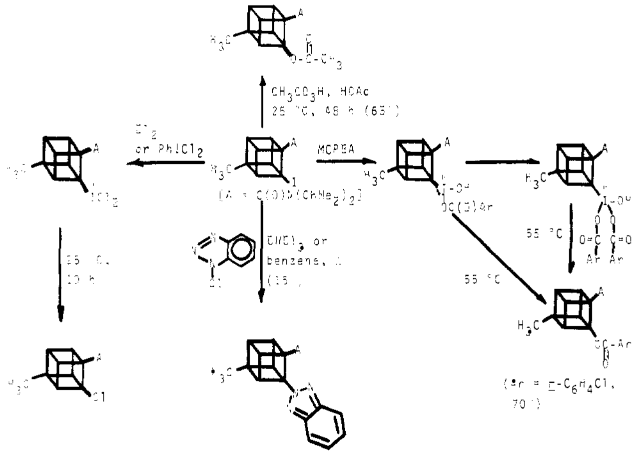


SCHEME 11



SCHEME 12

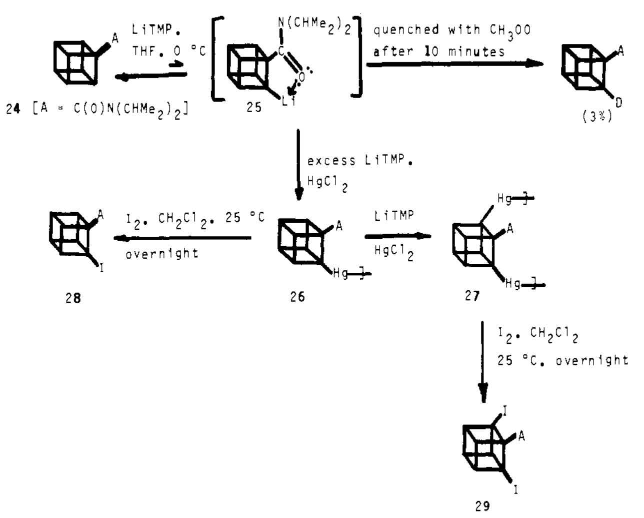


sequent conversion of 22c into the corresponding diester via reaction with 2-mercaptopyridine *N*-oxide followed by decomposition of this diester in bromotrichloromethane solvent[49] afforded octabromocubane (23), the first *perhalogenated* cubane (Scheme 10).

C. Direct Substitution on the Cubane Ring Skeleton. A Renaissance in Cubane Chemistry

Since the first substituted cubanes to have been synthesized were cubanecarboxylic and cubanedicarboxylic acids,[4,41] most of the early work on the synthesis of functionalized cubanes centered primarily around manipulation of the CO_2H functional group. Ultimate conversion of this moiety into other substituents frequently was accomplished by using a variety of more or less standard synthetic techniques.[43,50-54] More recently, iodinative decarboxylation has been utilized for the synthesis of iodocubanes (Scheme 11).[53-56] The iodocubanes thereby obtained can be oxidatively deiodinated (via relatively stable, intermediate hypervalent iodine species) to afford new, substituted cubanes (Scheme 12).[57] As noted in section II.B, in those cases where polyhalogenated cubanes were synthesized, the approach chosen for this purpose invariably employed halogen-containing precursors rather

SCHEME 13

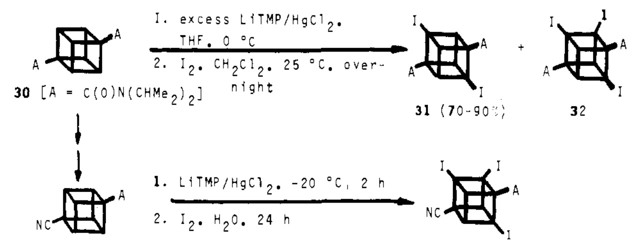


than proceeding via direct halogenation of the cubane nucleus.

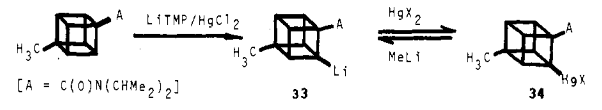
With the exception of the work described briefly above, interest in cubane synthesis waned between the mid-1970s and early 1980s. In particular, it has been known for many years that the acidity of cubane C–H bonds is comparable to that of C–H bonds in benzene and is significantly enhanced relative to the acidity of the corresponding C–H bonds in such simple strained ring systems as cyclopropane and cyclobutane.[58] Nevertheless, the possibility that this fact might be utilized advantageously to synthesize highly functionalized cubanes via direct substitution upon the cubane skeleton went largely ignored, probably for a variety of reasons.[59] This situation has changed dramatically in recent years, primarily due to Eaton's observation[59,60] that, under certain conditions, it is possible to directly metalate the cubane skeleton.[61] As a result, there has been a resurrection of interest in cubane and in the synthesis of substituted cubanes. Much of the impetus for revitalization in this regard stems from U.S. military interests in substituted (particularly polynitro-substituted) cubanes as a potentially important new class of energetic materials.[51,62]

Eaton's approach to direct functionalization of the cubane skeleton owes its genesis to earlier reports of heteroatom-directed ortho-lithiations in substituted aromatic systems.[63] Thus, in the reaction of cubane-*N*,*N*-diisopropylcarboxamide (**24**) with excess lithium tetramethylpiperidide (LiTMP, THF solvent, 0 °C), the tertiary amide functionality was found to direct "ortho"-lithiation to an adjacent carbon atom, thereby affording the corresponding complexed cubyllithium intermediate, **25**. This organometallic intermediate could be quenched with CH_3OD to afford monodeuterated **24** in ca. 3% yield. If instead intermediate **25** was generated in the presence of $HgCl_2$ (an electrophilic anion trap), mixtures of "ortho"-mercurated cubanes (e.g., **26** and **27**) resulted. When this mixture of mercurated products was quenched by reaction with elemental iodine, a mixture of mono- and diiodo derivatives of **24** (i.e., **28** and **29**, respectively) was formed. The foregoing reactions are summarized in Scheme 13.[59] More extensively iodinated cubane derivatives (i.e., **31** and **32**) could be synthesized by applying this same approach to cubane-1,4-bis(*N*,*N*-diisopropylcarboxamide) (**30**) as starting material (Scheme 14).[59]

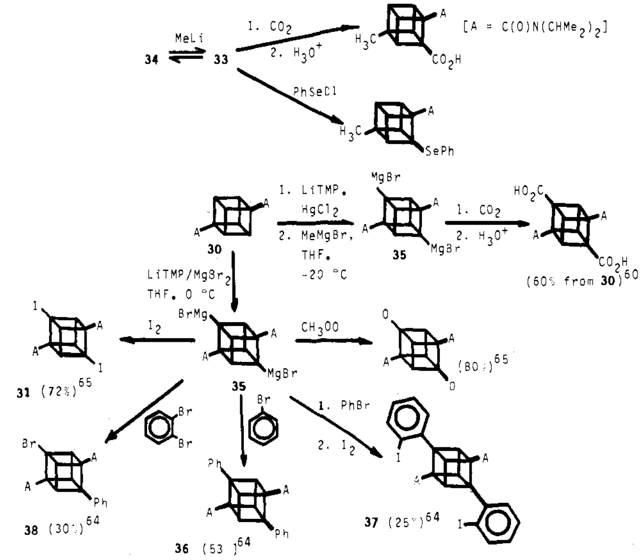
SCHEME 14



SCHEME 15



SCHEME 16



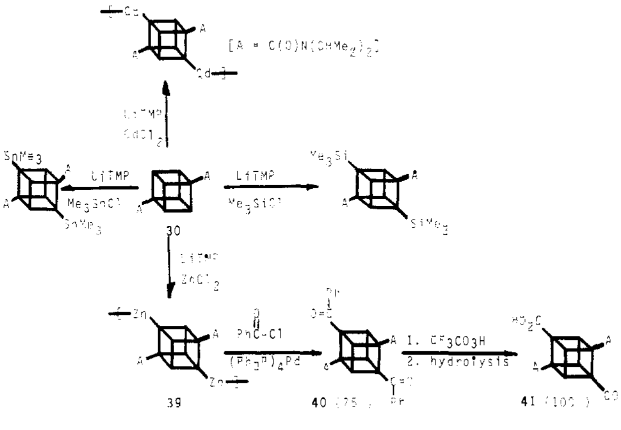
Subsequently, it was found that the transmetalation process by which cubyllithium compounds could be converted to the corresponding cubylmercury analogues[59] could be reversed.[60] Thus, treatment of cubylmercury derivative **34** with excess methyllithium resulted in equilibrium transmetalation with concomitant formation of **33** (Scheme 15).

Whereas the equilibrium (i.e., "instantaneous")[59] concentration of cubyl anion formed via direct lithiation of **24** was observed to be very low,[59] the corresponding equilibrium concentration of organolithium species (i.e., **33**) that results from the "reverse transmetalation" reaction of **34** with methyllithium is sufficiently high to render the organolithium species valuable as an intermediate for the synthesis of substituted cubanes. Thus, it proved possible to carry out the conversions indicated in Scheme 16.[60,64,65]

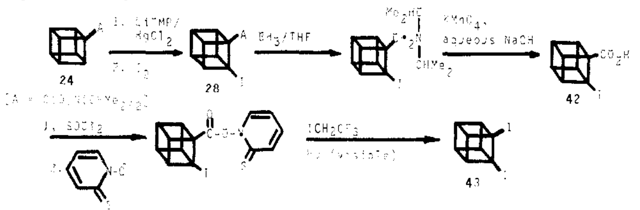
Of particular interest in Scheme 16 is the reaction of metallocubane intermediate **35** with bromobenzene, which affords the corresponding diphenylcubanediamide, **36**, in 53% yield. That this reaction proceeds via formation of a benzyne intermediate is indicated by the fact that a bis(*o*-iodophenyl) derivative, **37**, is obtained in 25% yield when the reaction mixture is quenched with elemental iodine.[64]

A variety of metalated cubanes have been synthesized via reaction of cubyl amides with LiTMP plus a metal halide [e.g., $ZnCl_2$, $CdCl_2$, $(CH_3)_3SnCl$, $(CH_3)_3SiCl$

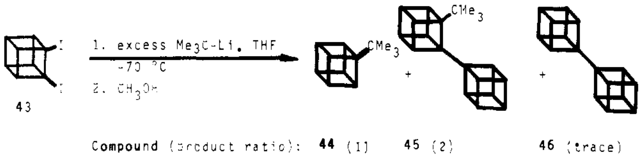
SCHEME 17



SCHEME 18



SCHEME 19



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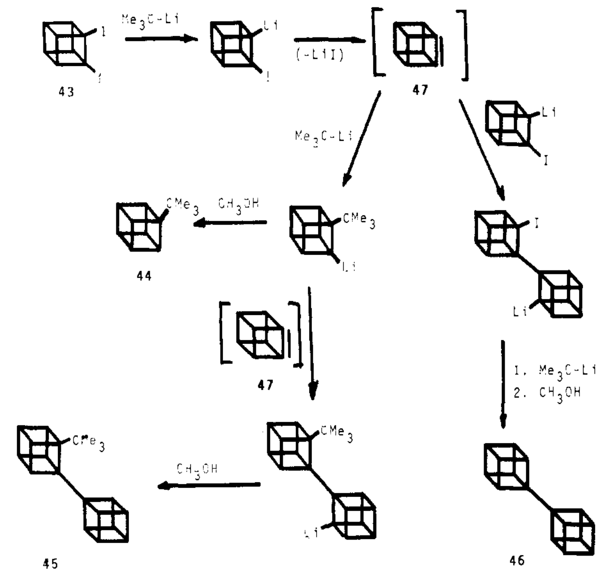
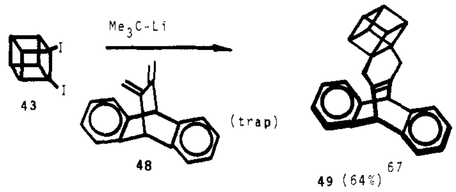


SCHEME 21



(Scheme 17)].[65] It was also shown that the cubylzinc intermediate **39** was capable of undergoing condensation with benzoyl chloride when the reaction was conducted in the presence of tetrakis(triphenylphosphine)palladium, thereby affording diketone **40** in 75% yield. Subsequent Baeyer–Villiger oxidation of **40** with trifluoroperacetic acid followed by hydrolysis afforded the first cubanetetracarboxylic acid derivative, **41**.[65]

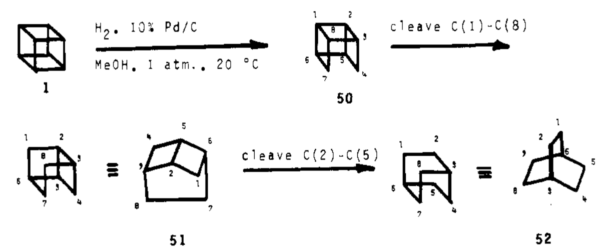
Although the ortho-directing ability of the *N*,*N*-diisopropylcarboxamido group is invaluable in promoting direct metalation of cubanes,[66] it was soon recognized that a major drawback to the use of this functionality is its resistance to hydrolysis under either acidic or basic conditions. This problem eventually was overcome by application of a two-step procedure that functions as a "hydrolysis equivalent", i.e., (i) reduction of the amido functionality in the substituted cubane-*N*,*N*-diisopropylcarboxamide with borane–tetrahydrofuran complex followed by (ii) oxidation of the resulting, substituted tertiary cubylcarbinyl amine with potassium permanganate in aqueous base. Application of this procedure to **28** afforded the corresponding iodocubanecarboxylic acid, **42**. This procedure is part of the multistep reaction sequence that was utilized by Eaton and Maggini to synthesize 1,2-diiodocubane (**43**) from **24** in 40% overall yield (Scheme 18).[67]

Iodocubane was found to undergo halogen–metal exchange when it was reacted with *tert*-butyllithium; only cubane was recovered when the reaction mixture was quenched with methanol. However, when the reaction of **43** with excess *tert*-butyllithium was performed in THF solution at −70 °C and then quenched by addition of methanol, two products, *tert*-butylcubane (**44**) and 2-(*tert*-butylcubyl)cubane (**45**), were obtained (ratio 1:2) along with a small amount of cubylcubane (**46**, Scheme 19).[67] Attempts to obtain a single crystal of **45** by slow evaporation of an *n*-octane solution resulted in cocrystallization of **45** and **46**. The structure of the cocrystallized material was elucidated by X-ray crystallographic analysis.[68] As a result of this study, it was shown that the intercage bond lengths in both **45** and **46** are unusually short (1.474 and 1.458 Å, respectively). This result most likely is a consequence of the unusually high percent s character in the exocyclic carbon orbitals in cubane.[58,69]

In order to account for the formation of **45** and **46** in the reaction of 1,2-diiodocubane with *tert*-butyllithium, a mechanism was suggested that invokes the intermediacy of 1,2-dehydrocubane ("cubene" (**47**), Scheme 20).[67] Analogy for the intermediacy of cubene in this reaction (and for the nucleophilic addition of *tert*-butyllithium to the highly pyramidalized carbon–carbon double bond in cubene) is provided by three separate observations: (i) Reaction of 1-bromo-4-chlorobicyclo[2.2.0]hexane with *n*-butyllithium affords 1-bromo-4-*n*-butylbicyclo[2.2.0]hexane.[70] (ii) Organolithium reagents are known to add to the carbon–carbon double bond in dehydroquadricyclanes and to bicyclo[1.1.0]but-1(3)-ene derivatives.[71] (iii) Butyllithium-promoted dehalogenation of 4-bromo-5-iodohomocubane results in formal replacement of *bromine* (not iodine) by an *n*-butyl group; the intermediacy of homocub-4(5)-ene has been suggested to account for this observation.[72]

Further evidence for the formation of cubene via reaction of **43** with *tert*-butyllithium is provided by the results of a trapping experiment. When **43** was reacted at room temperature with *tert*-butyllithium in benzene in the presence of diene **48**, the corresponding Diels–

SCHEME 22



Alder cycloadduct, **49**, was formed in 64% isolated yield (Scheme 21).[67] Although the result of the trapping experiment shown in Scheme 21 is consistent with Eaton and Maggini's interpretation,[67] it nevertheless does not provide unequivocal proof of the transient intermediacy of cubene in the reaction of **43** with *tert*-butyllithium. Unequivocal verification in this regard awaits more direct evidence of the kind that could be provided by spectral analysis of matrix-isolated cubene at exceedingly low temperatures.[73]

III. Reactions of Substituted Cubanes

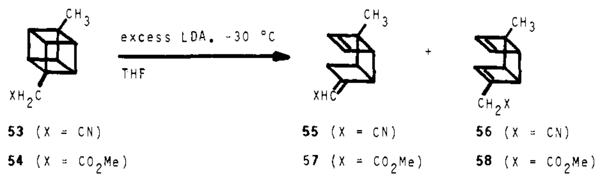
A. Cage Fragmentation Processes

The unusual thermal (i.e., kinetic) stability of cubane that belies its thermodynamic instability was mentioned in the Introduction. It has been pointed out that this apparent anomaly reflects the "inability of the cage molecule to undergo bond reorganization in a *concerted* manner in the ground state. When there is the possibility of reorganization via a *nonconcerted* process, a fast cage degradation or fragmentation reaction may take place, even at low temperatures".[38] In this section, we shall specifically consider cage-opening reactions (e.g., hydrogenolysis, base-promoted homoketonization, and thermal processes) that derive some driving force from the release of strain concomitant with cleavage of a carbon–carbon σ bond in the cubane system. One such example has already been discussed, i.e., in connection with Haller–Bauer cleavage that competes with base-promoted semibenzilic acid rearrangements of cage α-halo ketones (see section II.B).

Under appropriate conditions, it is possible to promote hydrogenolysis of a cubane C–C bond;[74] indeed, it has been suggested that hydrogenolysis of *three* cubane C–C bonds might occur under relatively mild conditions.[74] However, Stober and Musso[74] found that hydrogenolysis could be controlled to permit isolation of the product formed during uptake of 1 equiv of hydrogen. Thus, reaction of a methanol solution of cubane with hydrogen gas over 10% palladized charcoal catalyst at 20 °C resulted in the uptake of 1 equiv of hydrogen within ca. 2 h, thereby affording tetracyclo[4.2.0.$0^{2,5}$.$0^{3,8}$]octane ["secocubane" (**50**)] in high yield. When longer reaction times were employed, further reduction of **50** to tricyclo[4.2.0.$0^{4,7}$]octane ["nortwistbrendane" (**51**)] and to bicyclo[2.2.2]octane (**52**) gradually occurred (Scheme 22).[74b]

All C–C bonds in cubane are, of course, chemically equivalent; however, there are *six* nonequivalent cyclobutane C–C bonds in secocubane. Further hydrogenolysis of **50** should occur preferentially at the most strained (and, hence, the longest) carbon–carbon σ bond.[75] Therefore, it was of interest to examine the course of catalytic hydrogenolysis of **50** and to attempt to account mechanistically for the stepwise conversion **50** → **51** → **52**.

SCHEME 23



The results of force-field calculations[9,76] suggest that hydrogenolysis of **50** and of **51** occurs in each case (i) at the longest (and weakest) carbon–carbon bond and (ii) to afford the least highly strained product. The initial (kinetically controlled) hydrogenolysis of a cubane carbon–carbon bond that leads to the formation of secocubane (**50**) is accompanied by the release of ca. 50 kcal/mol of strain energy.[74b,75] Subsequent hydrogenolysis of the C(1)–C(8) bond in **50** (which results in the formation of **51**) is favored energetically vis-à-vis hydrogenolysis of the corresponding C(1)–C(2) bond in **50** (which would afford tricyclo[3.1.1.$1^{2,4}$]octane) by ca. 34 kcal/mol. Finally, hydrogenolysis of the most highly strained carbon–carbon bond in **51** produces bicyclo[2.2.2]octane with concomitant release of ca. 45 kcal/mol of strain energy.[74b]

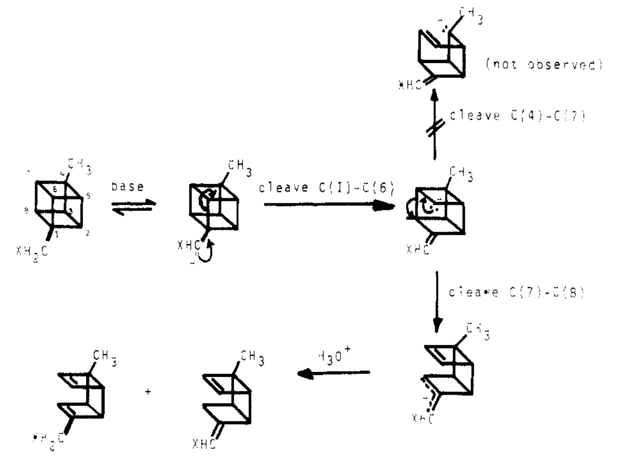
Base-promoted reactions of substituted cubanes that lead to ring opening (e.g., homoketonization[77] and homoallylic rearrangement processes[78]) have been studied. Thus, treatment of either 1-bromo-4-cubanol or the corresponding acetate with NaOMe or KOH in methanol resulted in instantaneous reaction with concomitant formation of a complex, intractable mixture of products.[77] It was suggested that this reaction proceeded via the corresponding intermediate bromosecocubanone, although this compound was neither isolated nor characterized.[78]

More fruitful results were obtained from a study of base-induced homoallylic rearrangements in (4-methylcubyl)acetonitrile (**53**) and methyl (4-methylcubyl)acetate (**54**).[78] Thus, treatment of **53** with excess lithium diisopropylamide (LDA) in dry tetrahydrofuran at −30 °C afforded an intractable mixture of two ring-opened alkenes (**55** and **56**). Similar results were obtained when **54** was reacted in this manner with LDA; esters **57** and **58** were thereby obtained in essentially quantitative yield (Scheme 23).[78]

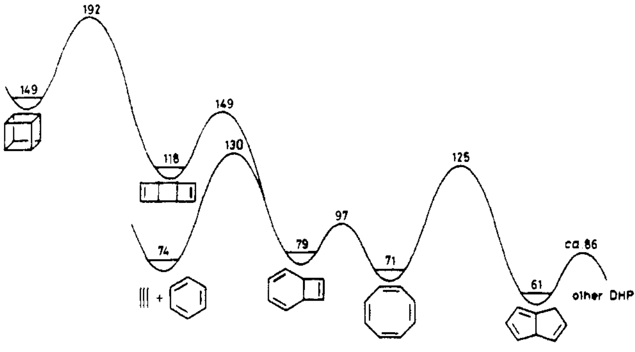
The homoallylic rearrangements shown in Scheme 23, in fact, are regiospecific processes. All three cyclobutane C–C bonds about C(1) [i.e., C(1)–C(2), C(1)–C(6), and C(1)–C(8)] are equivalent by symmetry. After initial cleavage of one of these three bonds occurs, a second cyclobutane carbon–carbon bond is broken regiospecifically to produce the corresponding (resonance stabilized) allylic carbanion. This process is illustrated in Scheme 24 for cleavage of the C(1)–C(6) bond followed by regiospecific cleavage of the C(7)–C(8) [rather than the C(4)–C(7)] bond. The sequence shown therein accounts for the observed course of the base-promoted reactions of **53** and **54** (Scheme 23).

The static pyrolysis of cubane has been studied by Martin and co-workers.[79,80] The products formed via pyrolysis in the temperature range 230–260 °C were found to be acetylene, benzene, cyclooctatetraene, styrene, and 1,2-, 1,4-, and 1,5-dihydropentalenes. In ad-

SCHEME 24



SCHEME 25[a]



[a] Reprinted from ref 80; copyright 1985 The Royal Society of Chemistry.

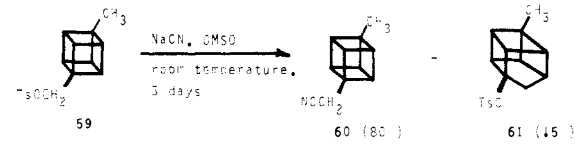
dition, a small amount of semibullvalene (tricyclo[3.3.0.0^{2,8}]octa-3,6-diene, which interconverts thermally with cyclooctatetraene) was detected among the thermolysis products.[79] The distribution of the various reaction products was found to be strongly pressure dependent; benzene and acetylene were the predominant products at low pressures, whereas cyclooctatetraene predominated at high pressures. This result was considered to provide evidence for the intermediacy of vibrationally excited cyclooctatetraene in the thermal decomposition of cubane. The thermochemistry of cubane rearrangement is summarized in the hypersurface shown in Scheme 25.[80]

The rate-determining step in the thermal decomposition of cubane is believed to involve simple homolysis of one of the skeletal carbon–carbon bonds, thereby affording a diradical in which most of the original cage skeleton remains intact.[80] This process results in release of a relatively minor amount of strain energy (thus accounting for the unusually high thermal stability of cubane). Further fragmentation of this diradical follows the pathway summarized in Scheme 25. The strain energy originally contained within the cubane framework is expressed ultimately as excess vibrational energy in cyclooctatetraene.[80]

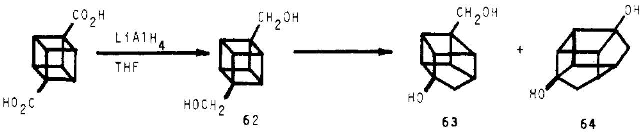
B. Ring-Expansion Processes

In the foregoing examples, relief of strain energy contained within the cubane framework provides the driving force for fragmentation of the cage system. An alternative and less disruptive means to relieve strain in cubanes might involve ring expansion rather than ring fragmentation. This expectation has been realized via reactions of cubylcarbinyl derivatives. Thus, treatment of a dimethyl sulfoxide solution of cubylcarbinyl tosylate **59** with sodium cyanide affords the corresponding unrearranged nitrile, **60**, along with a small amount of homocubyl tosylate **61**.[78] Compound **61** most likely is formed by a competing solvolytic process that results in formation of a homocubyl carbocation which in turn is trapped by internal return of tosylate. Although precautions were taken, it was not possible to avoid formation of **61** in this reaction (Scheme 26).[78]

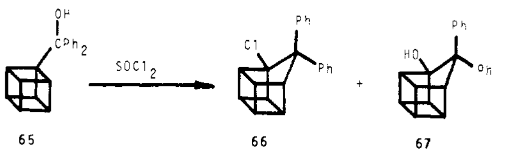
SCHEME 26



SCHEME 27



SCHEME 28



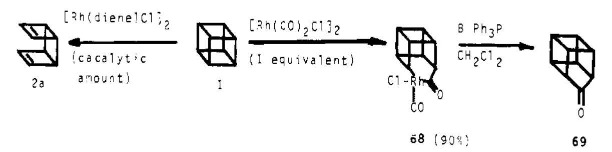
Edwards and co-workers[43d] encountered a similar problem when they attempted to reduce a tetrahydrofuran solution of cubane-1,4-dicarboxylic acid with lithium aluminum hydride. Isolation of the desired diol, **62**, was complicated by its facile solvolytic isomerization to the corresponding homocubanol and 1,3-bishomocubanediol derivatives [i.e., **63** and **64**, respectively (Scheme 27)].[43d]

A final example is provided by the reaction of cubyldiphenylcarbinol (**65**) with thionyl chloride. This reaction has been reported to afford the corresponding rearranged chloride, **66**, and the rearranged alcohol, **67**, that results via internal return (Scheme 28).[81]

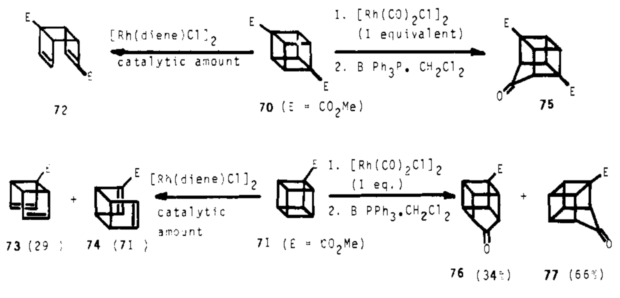
C. Transition-Metal-Promoted Valence Isomerizations

The use of transition metals to perform valence isomerizations in strained molecules is well documented.[82] Cubanes react avidly with a number of transition-metal salts and/or organometallic complexes [e.g., salts and/or complexes of rhodium(I),[83] silver(I),[84,85] and palladium(II)[85]]. Reaction of a chloroform or carbon tetrachloride solution of cubane (or of a substituted cubane) with a catalytic amount of a [Rh(diene)Cl]$_2$ complex results in rapid, quantitative conversion of the substrate to the corresponding *syn*-tricyclo[4.2.0.0^{3,5}]octa-3,7-diene. If instead this reaction is performed by using a stoichiometric amount of [Rh(CO)$_2$Cl]$_2$, oxidative addition to a C–C σ bond occurs with concomitant formation of a stable acylrhodium complex, **68**.[83] Such oxidative additions of d^8 complexes to C–C σ bonds are well-known.[86] Treatment of **68** with

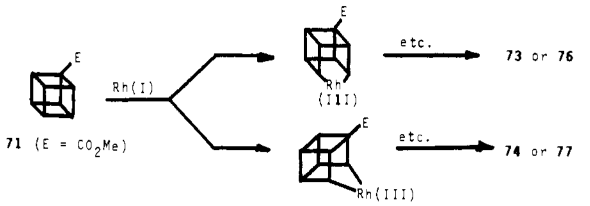
SCHEME 29



SCHEME 30



SCHEME 31



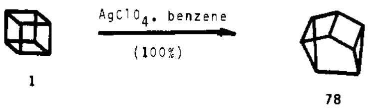
a stoichiometric amount of triphenylphosphine results in ligand exchange with concomitant formation of homocubanone [69 (Scheme 29)].[83]

The corresponding reactions of dimethyl 1,4-cubanedicarboxylate (**70**) and of methyl cubanecarboxylate (**71**) with Rh(I) complexes also have been studied. Thus, treatment of **70** with a catalytic amount of a $[Rh(diene)Cl]_2$ complex afforded **72**. Similar reaction of **71** yielded two products [i.e., **73** (29%) and **74** (71%) (Scheme 30)].

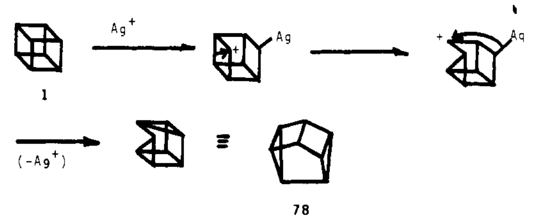
When the rearrangement of a chloroform solution of **71** was conducted at 40 °C by using $[Rh(norbornadiene)Cl]_2$ as catalyst, the rearrangement to **73** and **74** was observed to occur 16 times more slowly than the corresponding rearrangement of cubane.[83] The major product of the Rh(I)-promoted valence isomerization of **71** (i.e., **74**) is that diene which is formed via cleavage of the carbon–carbon σ bond that bears the electron-withdrawing carbomethoxy group. In addition, reaction of **70** with a stoichiometric amount of $[Rh(CO)_2Cl]_2$ followed by breakup of the intermediate acylrhodium complex thereby obtained with a stoichiometric amount of triphenylphosphine afforded the corresponding disubstituted homocubanone, **75**. Similar treatment of **71** afforded a mixture of two monosubstituted homocubanones [i.e., **76** (34%) and **77** (66%) (Scheme 30)].[83]

Interestingly, the distribution of dienes formed from the catalytic reaction of Rh(I) with methyl cubanecarboxylate (i.e., **71** → **73** + **74**) is in good semiquantitative agreement with the corresponding product distribution that results from oxidative addition of Rh(I) to methyl cubanecarboxylate in the corresponding stoichiometric reaction (i.e., **71** → **76** + **77**). This observation suggests that a common set of organorhodium(III) intermediates is involved in the formation of both sets of products. Furthermore, it is likely that the competition between these two pathways is "governed by the same (approximately statistical) competition between the two alternative sterically favored modes of oxidative addition of **71**" (Scheme 31).[83]

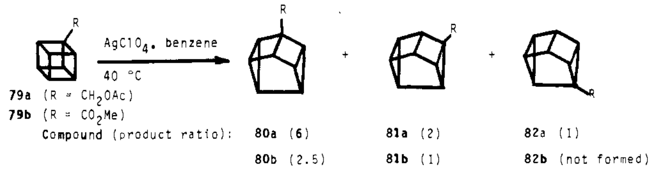
SCHEME 32



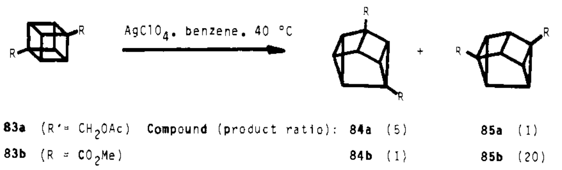
SCHEME 33



SCHEME 34



SCHEME 35



The corresponding reactions of cubane (and of substituted cubanes) with Ag(I) and with Pd(II) follow a radically different pathway. Thus, reaction of a benzene solution of cubane with $AgClO_4$ affords cuneane (**78**) rapidly and quantitatively (Scheme 32).[85]

Both Ag(I) and Pd(II) display a diminished tendency to undergo either oxidation or oxidative addition vis-à-vis Rh(I). Instead, the metal catalyst in Ag(I)- or Pd(II)-catalyzed reactions with strained alkanes interacts essentially as a Lewis acid with the strained carbon–carbon σ bond in the substrate (which serves as an electron donor). Consistent with this formalism, the logarithm of the rate constants for Ag(I)-catalyzed cubane → cuneane rearrangements in 1,4-disubstituted cubanes has been found to afford a good-quality linear correlation with the sum of the Taft σ^* polar substituent constants for the 1,4-substituents, the slope of which is *negative* (i.e., $\log k = -1.35\sigma^* + 0.80$, correlation coefficient -0.987).[84] Presumably, the presence of electron-withdrawing substituents interferes with the electron-donating ability of the carbon–carbon σ bonds in the cubane, thereby impeding rate-determining attack by Ag(I) upon the substrate. A mechanism that is capable of rationalizing the course of the cubane → cuneane rearrangement is shown in Scheme 33.[87]

Silver(I)-promoted rearrangement of monosubstituted cubanes **79a** and **79b** has been studied.[85,88] Thus, reaction of **79a** with silver perchlorate in benzene at 40 °C affords all three possible cuneanes (**80a**, **81a**, and **82a**; product ratio 6:2:1), whereas the corresponding rearrangement of **79b** affords only two isomeric cuneanes [**80b** and **81b**; product ratio 2.5:1 (Scheme 34)].[85]

TABLE 1. Coupling Constants ($^nJ_{XY}$) in Substituted Cubanes (C_8H_7R)

compd	n	X	Y	$^nJ_{XY}$, Hz	ref
1 (R = H)	1	C	H	160 ± 5	4
	1	C	H	153.8 ± 0.6	89a
86 (R = $^{13}CO_2H$)	1	C	C	64.36 ± 0.05	90
	2	C	C	2.29 ± 0.05	
	3	C	C	2.69 ± 0.05	
	4	C	C	0.78 ± 0.05	
87 (R = $^{13}CH_3$)	1	C	C	37.0 ± 0.1	91
	2	C	C	2.03 ± 0.02	
	3	C	C	2.58 ± 0.02	
	4	C	C	0.51 ± 0.02	
88 (R = $SiMe_3$)	1	C	Si	not obsd	61
	2	C	Si	2.44 ± 0.02	
	3	C	Si	3.32 ± 0.02	
	4	C	Si	no coupling detected	

The corresponding Ag(I)-promoted valence isomerizations of 1,4-disubstituted cubanes have also been studied. The results thereby obtained are summarized in Scheme 35.[85]

The results of a study of the relative rates of Ag(I)-promoted rearrangements of **79a**, **79b**, **83a**, and **83b** indicate that substitution on the cubane skeleton by one acetoxymethyl or carbomethoxy substituent or by two such substituents located in the 1,4-positions results in a pronounced retardation in the rate of valence isomerization to cuneanes. This rate-retarding effect of substituents is greatest when electron-withdrawing groups are present on the cubane skeleton.[85]

IV. Miscellaneous Studies Involving Cubanes

A. Spectral and Physical-Organic Studies of Cubanes

As noted previously, nuclear magnetic resonance spectroscopic measurements provided the first experimental information regarding the hybridization of a skeletal carbon atom in cubane.[58,89] More recently, Della and co-workers have measured $^nJ_{CC}$ values for n = 1–4 in cubanecarboxylic-*9*-^{13}C acid (**86**)[90] and in methylcubane-*9*-^{13}C (**87**).[91] In addition, $^nJ_{CSi}$ coupling constants in (trimethylsilyl)cubane (**88**) have been reported.[61] These results are summarized in Table 1.

The methine carbon-13 shielding tensor in cubane has been measured at low temperature (ca. 20 K) in a static sample of solid cubane.[92] This shielding tensor was also calculated and analyzed (with regard to individual diamagnetic and paramagnetic bond contributions to total shielding) by using the individual gauge localized orbitals (IGLO) method.[93] In this way, insight into the factors that determine the observed chemical shift of the cubane methine carbons and the relationship of this quantity to the molecular structure of cubane could be gained.[94]

Proton magnetic resonance spectra of mono- and 1,4-disubstituted cubanes have been reported.[95] Proton–proton coupling constants extracted from the $(AB)_3$ spectra obtained for 1,4-disubstituted cubanes over the range of substituents studied were as follows: $^3J_{AB}$ (="J_{ortho}") = (5.0–5.6) ± 0.1 Hz; $^4J_{AA'}$ and $^4J_{BB'}$ (="J_{meta}") = (2.0–3.4) ± 0.2 Hz; $^5J_{AB}$ (="J_{para}") = (−0.35 to −1.36) ± 0.2 Hz.[92] The magnitudes and signs (both positive) of the $^3J_{HH}$ and $^4J_{HH}$ couplings are in accord with expectations based upon analysis of bond geometries (i.e., torsion angles) and upon the existence of a roughly planar "W" pathway that links the "meta" protons in these 1,4-disubstituted cubanes. The small negative $^5J_{HH}$ that was observed between "para" protons in this system is unusual and was considered to reflect "through-space" transmission of spin information[96] via back-lobe orbital overlap that occurs through the interior of the cubane skeleton.

Both proton chemical shifts and proton–proton coupling constants were found to vary with substituent electronegativity in mono- and 1,4-disubstituted cubanes.[95] Interestingly, the magnitude of "ortho" couplings in 1,4-disubstituted benzenes increased in roughly linear fashion with increase in the sum of the electronegativities of the 1- and 4-substituents (i.e., as reflected by the sum of the values of Taft's substituent constants, σ_i, of the 1,4-substituents). In contrast to this behavior, the corresponding "para" coupling was observed to become more negative with increasing σ_i. No clear trend was reflected by the observed variation of the corresponding "meta" proton–proton coupling constants with substituent electronegativities. Finally, aromatic solvent-induced shifts (ASIS) of substituted cubanes measured in benzene and in pyridine were found to be clearly additive.[95]

In subsequent work, proton NMR chemical shifts and proton–proton coupling constants in substituted 4-bromohomocubanes were found to correlate with the corresponding chemical shifts and coupling constants in cubanes.[97] The results were considered to provide evidence for a "through-space mechanism for both cross-ring coupling and the transmission of substituent effects in these systems".[97] The results of complementary studies of acid dissociation constants of 4-substituted cubane-1-carboxylic acids[98] were rationalized in terms of the Kirkwood–Westheimer field model[99] for propagation of polar substituent effects in saturated systems.

Photoelectron (PE) spectroscopy has been utilized to study the electronic structure of cubane and of substituted cubanes. Due to the high symmetry of cubane, the highest occupied molecular orbitals (MOs) of cubane comprise a triply degenerate $3T_{2g}$ set followed by a triply degenerate subjacent $1T_{2u}$ set.[100,101] Cubane possesses a low first ionization energy (vertical: 9.0–9.1 eV;[100,102] adiabatic: 8.74 eV[103,104]). Concomitant with this low ionization energy, cubane also can be oxidized electrochemically with relative ease ($E_{1/2}$ vs SCE = 1.73 V).[105]

By substituting cubane in the 1,4-positions with halogen atoms, the molecular symmetry is reduced from O_h to D_{3d}. Accordingly, much of the orbital degeneracy noted for cubane is removed in 1,4-dihalocubanes, and, consequently, the resulting PE spectra of 1,4-dihalocubanes are considerably more complex than that of cubane. Cubane is unusual in that there is a large, band-free gap in its PE spectrum between the $3T_{2g}$–$1T_{2u}$ orbital pairs at ca. 9–10.5 eV and the E_g–T_{1u} orbital pairs at ca. 13.5–14.5 eV. It happens that 1,4-dichloro- and 1,4-dibromocubane each possess np atomic orbital basis energies which fall within this ca. 3 eV gap, and which, therefore, can interact hyperconjugatively with both sets of orbital pairs. Whereas interaction with the lower lying set ($3T_{2g}$–$1T_{2u}$) leads to destabilization ("normal" hyperconjugation), the corresponding interaction with the higher energy set (E_g–T_{1u}) results in stabilization ("inverted" hyperconjugation). Accordingly, the lone-pair ionization energies of 1,4-dichloro- and of 1,4-dibromocubane are higher than would be expected in the absence of this effect, with the net result that essentially no shift of the bands associated with lone-pair ionization occurs in their PE spectra.[106]

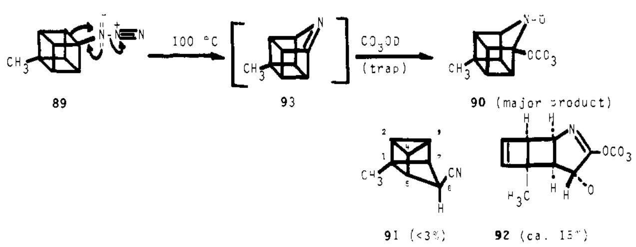
Vibrational spectra of cubane and substituted cubanes have been examined in several laboratories. Della and co-workers[107] have assigned the fundamental vibrational modes in cubane and in four specifically deuterated cubanes; a total of 120 modes were assigned. Despite the high degree of C–C–C angle strain present at each cubane vertex, no unusual features were noted in the infrared spectra of these compounds that might have resulted therefrom. In a later study, the infrared-active fundamental vibrational modes of cubane were measured in the gas phase at Doppler-limited resolution by using tunable laser instrumentation.[108] Analysis of the gas-phase data thereby obtained permitted calculation of the following bond lengths in cubane: C–H bond, 1.11 (2) Å; C–C bond, 1.565 (4) Å.[108] These values are somewhat larger than the corresponding average crystallographic bond lengths determined for (solid) cubane, [i.e., C–H bond, 1.06 (7) Å; C–C bond, 1.551 (5) Å].[6a]

The vapor-phase infrared spectrum and condensed-phase Raman spectrum of cubane also have been reported.[109] In addition, semiempirical[92] and ab initio[110] theoretical studies of the vibrational structure of cubane have appeared.

The mass spectrum of cubane has been studied under a variety of experimental conditions.[7] Gross[111] has reported ionization and appearance potentials of cubane as determined by ion cyclotron resonance (ICR). The appearance potential of the $(C_6H_6)^+$ fragment ion was found to be 9.2 eV, in agreement with the corresponding value that had been obtained earlier by using conventional electron impact techniques.[112] More recently, Lifshitz and Eaton[113a] found evidence in the mass spectral fragmentation pattern of cubane[113b] that suggests that the parent $(C_8H_8)^+$ ion does not isomerize to either cyclooctatetraene or styrene prior to dissociation.

The cubane radical cation, $C_8H_8^+$, has been generated by photoionization of cubane at 16.8 eV, and the electron spin resonance (ESR) spectrum of the free ion has been obtained in neon matrices at 4 K.[113c] Interestingly, the hydrogen hyperfine lines in the ESR spectrum thereby obtained indicate that all hydrogen atoms in the ion are equivalent on the ESR time scale. Rather than to postulate that the eightfold symmetry of cubane is preserved in the cubane radical cation, it was suggested instead that the cation undergoes rapid dynamic Jahn–Teller distortion at low temperature in neon matrices.[113c]

SCHEME 36



Paquette and co-workers[114] have studied the gas-phase basicities of cubane, dodecahedrane, and methylated dodecahedranes by using Fourier transform ICR spectrometry. Qualitatively, cubane was found to be more basic than isopropyl ether but less basic than α-methylstyrene under these conditions. The basicity of cubane, although quite high for a saturated hydrocarbon, nevertheless is considerably less than would be anticipated simply on the basis of bond strain considerations. Of particular interest is the fact that the dodecahedranes, which contain only about 17% as much strain energy per carbon as cubane,[114] possess basicities that are comparable to that of cubane. The high basicity of dodecahedrane is considered to reflect its high molecular polarizability (which is ca. 2.5 times greater than that of cubane).[114] The results of preliminary semiempirical (MNDO) and ab initio (HF/3-21G) calculations suggest that the most probable site for protonation of cubane is at one of its eight vertices.[115]

The cubyl radical has been generated by thermolysis of *tert*-butyl cubanepercarboxylate at 80 °C.[116] In the same study, the selectivity of the cubyl radical was gauged (i) by examination of the product distribution obtained via Hunsdiecker reaction of cubanecarboxylic acid in carbon tetrachloride and (ii) by examination of competitive reactions of the radical produced via perester thermolysis with CCl_4–$BrCCl_3$ solution.[116] The rate of formation of the cubyl radical via perester themolysis was found to be only $^{1}/_{4600}$th that of the *tert*-butyl radical under the same conditions. Not surprisingly,[117] the cubyl radical displayed low selectivity in the halogen atom abstraction reactions as compared with the results of corresponding reactions of other acyclic and monocyclic aliphatic radicals.[116] However, if comparison is restricted among corresponding reactions of other *bridgehead* radicals, then the cubyl radical actually appears to display relatively *high* selectivity. The finding that the least sterically hindered bridgehead radicals (such as cubyl radical) are the most selective runs contrary to that which has generally been observed for corresponding reactions of nonbridgehead radicals.[117] The results obtained for the cubyl radical are considered to reflect alterations in the transition state of bridgehead radical abstraction reactions concomitant with novel hybridization effects (vis-â-vis the corresponding reactions of nonbridgehead radicals).[116]

Finally, mention should be made of an interesting result that was obtained from a study of the thermal decomposition of 4-methyl-1-azidocubane (**89**). Facile decomposition of **89** in CD_3OD occurred at 100 °C in <1 h, thereby affording a ring-expanded amine, **90**, along with two other products, **91** and **92** (Scheme 36).[118] The intermediacy of "azahomocubene" **93** was suggested on the basis of the isolation of **90** as the major reaction product. Intermediate **93** is expected to be a highly energetic species since it contains an anti-Bredt imino C=N double bond which is highly deformed (i.e., twisted).

In contrast to this result, direct photolysis of a solution of **89** in either methanol-d_4 or dichloromethane-d_2 with Pyrex-filtered UV radiation afforded 1-methyl-*endo*-6-cyanotetracyclo[3.2.0.0^{2,4}.2^{3,7}]heptane (**91**, a substituted homoprismane) as the major product (60–80% yield).[118] It was suggested that **91** might be formed in this reaction either (i) directly from the starting azide, **89**, or (ii) indirectly via further photochemical rearrangement of initially formed intermediate

TABLE 2. **Results of Theoretical Calculations on the Molecular Structure and Energetics of Cubane 1**

method	HCH bond angle, deg	r_{C-C}, Å	r_{C-H}, Å	ΔH, kcal/mol	strain energy, kcal/mol	ref
molecular mechanics, Schleyer force field				148.59	165.9	9
molecular mechanics, Allinger force field				149.66	166.9	9
molecular mechanics (MM2)	125.26	1.557	1.114	148.9		128
molecular mechanics (MM2)	125.3	1.557		148.8		129
MINDO/3		1.568	1.105			100
IMOA		1.552	1.089			123b
self consistent field (SCF)		1.572	1.078			126
ab initio, STO-3G basis set		1.561	1.081			100
ab initio, STO-3G basis set		1.562	1.087			130
ab initio, STO-3G basis set	125.3	1.561	1.086			131
ab initio, 3-21G basis set	125.26	1.577	1.074	145.1		128, 132, 133
ab initio, 4-31G basis set	125.3	1.572	1.076			127
ab initio, 4-31G basis set		1.573	1.075			130
ab initio, 6-31G* basis set	125.26	1.557	1.114	148.9		128, 132, 133
ab initio, 6-31G* basis set	125.3	1.559	1.081	148.5	164.9	131

93. The results obtained via photolysis of **89** at 12 K in either a solid argon or 3-methylpentane matrix suggest strongly that the former is the more likely of these two mechanistic alternatives.[118]

B. Theoretical Studies of Cubanes

It is perhaps to be expected that the existence of so highly strained and symmetrical a molecule as cubane might present a siren call to theoreticians. Nevertheless, relatively few theoretical studies on cubane were undertaken prior to the late 1970s.[119] However, a number of theoretical studies on cubane of varying levels of sophistication (and expense) have been undertaken more recently. To conclude this review of the synthesis and chemistry of cubanes, a brief survey of such theoretical studies will be made.

One of the first features to be scrutinized by theoreticians was the unusually high strain energy in cubane. Simple additivity considerations[120] suggest that the total strain energy in cubane should be roughly 6 times the strain energy in cyclobutane, as has indeed been found to be the case.[7] Early MINDO/1 calculations incorrectly predicted a negative deviation from additivity for the strain energy of cubane.[121,122] More accurate estimation of the strain energy in cubane has been obtained by using the "iterative maximum overlap approximation" (IMOA) that relies upon an "sp^n hybridization model" of chemical bonding that employs variable, nonintegral values of n.[123] In another study, the results of extended-Hückel calculations revealed the existence of "bent bonds" in cubane in which maximum electron density was found to lie outside the vectors that join contiguous carbon atoms.[124] Molecular mechanics calculations (MM2, performed by using Allinger's force-field model)[125] afford a value of the heat of formation of cubane (i.e., 148.84 kcal/mol) that is in excellent agreement with the experimental value of 148.70 kcal/mol.[7]

Self-consistent-field (SCF) molecular orbital calculations have been utilized to investigate bond distances and ionization potentials in cubane.[126] The calculated carbon–carbon and carbon–hydrogen bond lengths thereby obtained are slightly longer than the values obtained by X-ray crystallography[6a] but are in excellent agreement with the corresponding values obtained via gas-phase electron diffraction.[108]

The results of ab initio Hartree–Fock (HF) calculations on the cubyl radical (performed by using a split-valence 4-31G basis set)[127] suggest that the cubic symmetry so characteristic of the parent hydrocarbon is lost in the corresponding radical. The calculated length of the carbon–carbon bonds that are adjacent to the radical site in the cubyl radical (i.e., α-C–C bonds, 1.562 Å) is shorter than that calculated for a C–C bond in cubane (i.e., 1.572 Å). However, the corresponding length of the β-C–C bonds in the cubyl radical (i.e., 1.577 Å) is *longer* than that calculated for a cubane C–C bond.

A representative (but by no means exhaustive) sampling of results of theoretical calculations on various aspects of the molecular structure and energetics of cubane is summarized in Table 2.[9,100,123b,126–133] Comparison of the calculated values shown in Table 2 with the corresponding experimental values[6a,7,8a] that have been cited earlier in this review will afford a measure of the reliability of each of the various theoretical approaches. The quality of agreement between theory and experiment is generally quite high.

Finally, the recent surge of interest in nitro-substituted cubanes as potential new high-energy materials[51,62] has provided impetus for theoretical investigations of polynitrocubanes. The results of ab initio calculations on $C_8H(NO_2)_n$ (n = 2–8) suggest that successive substitution of C–H bonds in cubane by NO_2 substituents leads to an increase in stability of the cubane skeleton.[134] In addition, electron density distributions in nitrocubanes have been calculated.[135]

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