Chem. Rev. **1989**, *89*, 1011–1033

Synthesis and Chemistry of Homocubanes, Bishomocubanes, and Trishomocubanes

ALAN P. MARCHAND

Department of Chemistry, University of North Texas, Denton, Texas 76203

Received October 26, 1988 (Revised Manuscript Received April 25, 1989)

Contents

I. Introduction

In recent years, saturated polycyclic "cage" molecules have held a special fascination for organic chemists. With the exception of adamantane, most saturated cage molecules contain considerable strain energy as evidenced by the fact that they (i) contain unusually long framework carbon–carbon σ-bonds, (ii) contain unusual C–C–C bond angles that deviate significantly from 109.5°, (iii) possess unusually negative heats of combustion, and (iv) possess unusually positive heats of formation when compared with nonstrained systems. Frequently, the strain energy contained within cage molecules also expresses itself through unusual patterns of chemical reactivity.[1] Additionally, the thermodynamic instability that this strain energy confers upon cage systems is a potential problem that synthetic organic chemists must learn to deal with constructively.

Alan P. Marchand, a native of Cleveland, OH, is a member of Local 72, American Federation of Musicians.

In this review, we shall focus upon the synthesis and chemistry of three types of *noncyclopropanoid* cubane[2] homologues that result via introduction of one ["homocubane" (**1**)], two ["bishomocubanes" (**2**–**6**)], and three methylene groups ["trishomocubanes" (**7**–**20**)] into the cubane skeleton. A listing of pertinent parent hydrocarbon structures appears in Table 1. No systematic attempt has been made in this review to cover functional group transformations of these cage systems. Coverage of the literature extends through August 1988.

II. Homocubanes (Pentacyclo$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$nonanes)

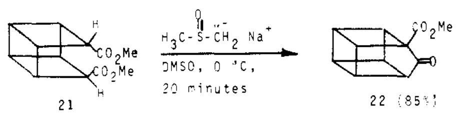
A. Syntheses of Homocubanes

Several independent syntheses of substituted homocubanes have been reported. In general, two types of approaches have proved successful in this regard: (i) intramolecular [2 + 2] photocycloadditions in appropriately substituted tricyclic diene systems[3-6] and (ii) ring contractions of appropriately substituted bishomocubanes.[7-13] Some examples of each type of synthesis are shown in Tables 2 and 3. In addition, Dieckmann condensation in a secocubane diester, i.e., **21**, has been found to be useful for synthesizing the corresponding substituted homocubane (i.e., **22**, Scheme 1).[14]

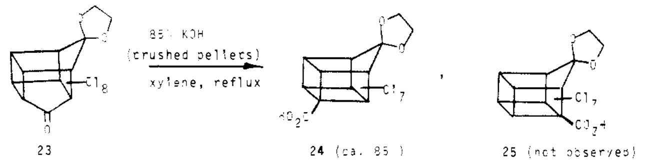
It is worthwhile to consider ring contractions as a general approach for synthesizing homocubanes (Table 2) and other cage compounds.[15] Whereas simple cyclic and acyclic α-halo ketones undergo Favorskii-type rearrangements[16] in the presence of base, cage α-halo ketones undergo a base-promoted rearrangement that is formally analogous to the corresponding base-pro-

0009-2665/89/0789-1011$06.50/0

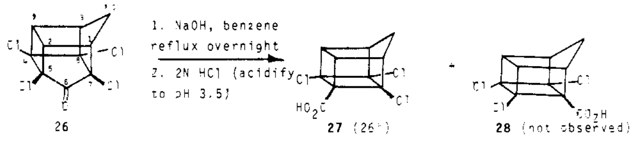
SCHEME 1



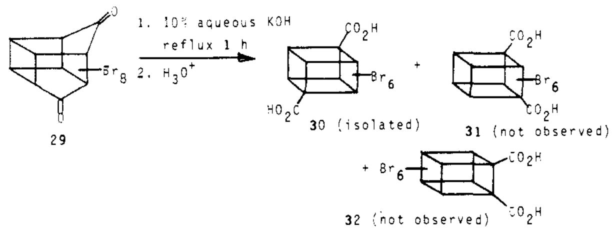
SCHEME 2



SCHEME 3



SCHEME 4

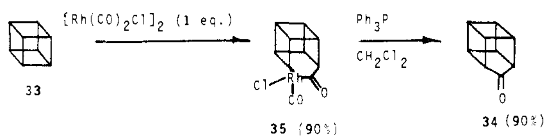


moted rearrangement of benzil to benzilic acid.[17] As in the case of the Favorskii rearrangement, this "semibenzilic acid" rearrangement results in ring contraction with concomitant formation of a carboxylic acid (or ester). Although this reaction is generally useful, several examples that might at first glance appear to be suitable for synthesizing substituted homocubanes nevertheless have been found to be impractical.[15] When they occur, deviating pathways that involve Haller-Bauer type cleavage[18] generally proceed with scission of a strained carbon–carbon σ-bond in the cage system. Examples of such deviant reactions in substituted homocubanes and in substituted 1,3-bishomocubanes (which might have served as precursors to the corresponding substituted homocubanes) are shown in Table 4.

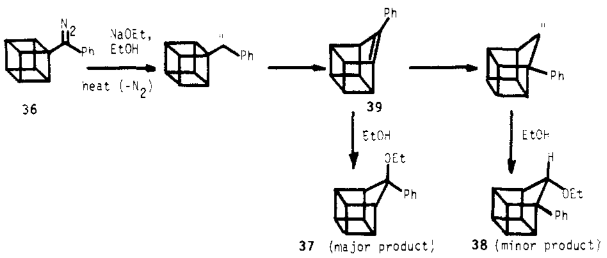
Some examples have been reported wherein semibenzilic acid rearrangements in unsymmetrically substituted cage systems occur regiospecifically, thereby affording a single ring-contracted product where more than one such product might have been formed. One such example, reported by Scherer and co-workers (i.e., regiospecific base-promoted ring contraction of **23** to **24**), is shown in Scheme 2.[13] A closely related example has also been reported (i.e., base-promoted conversion of **26** to **27**, Scheme 3).[9,10] In this same vein, Griffin and co-workers[19] have reported that semibenzilic acid rearrangement of octabromo-1,3-bishomocubanedione (**29**) affords only one of the three possible isomeric hexabromocubanedicarboxylic acids (i.e., **30**, Scheme 4). No convincing arguments have been forwarded to account for the unusual regioselectivity of each of the semibenzilic acid rearrangements **23** → **24**, **26** → **27**, and/or **29** → **30** cited in Schemes 2–4.

Substituted homocubanes also have been prepared by reaction of transition-metal complexes with cubane

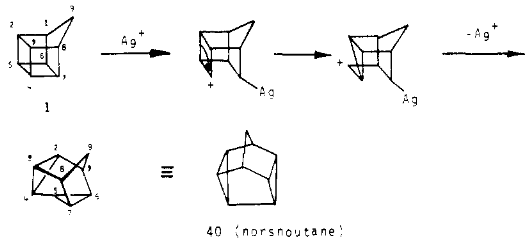
SCHEME 5



SCHEME 6



SCHEME 7



(see section I.B). Thus, reaction of cubane (**33**) with a stoichiometric amount of $[Rh(CO)_2Cl]_2$ affords homocubanone (**34**). A stable acylrhodium intermediate, **35**, has been isolated in this reaction (Scheme 5).[20]

Substituted homocubanes have been synthesized via carbene-mediated ring expansions performed in appropriately substituted cubanes. Thus, thermolysis of diazoalkane **36** in ethanolic sodium ethoxide afforded a 3:2 mixture of isomeric ethers (**37** and **38**, respectively). The intermediacy of 1-phenyl-9-homocubylidene in this reaction (and, by implication, 9-phenyl-1(9)-homocubene (**39**)), has been suggested (Scheme 6).[21]

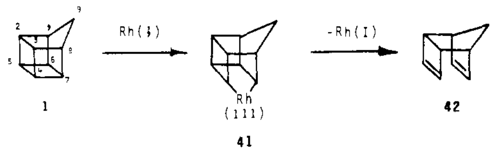
B. Reactions of Homocubanes

Much of the chemistry of homocubane and its derivatives is a natural consequence of the high level of strain energy contained within the homocubane skeleton. The results of force field calculations suggest that the strain energy of homocubane is on the order of 125 kcal/mol.[22] Thus, relief of strain provides an important driving force for Haller–Bauer type cleavage[18] that is encountered occasionally in base-promoted reactions of cage α-halo ketones (see Table 4).

The results of ab initio calculations reveal that significant negative electrostatic potentials are associated with strained carbon–carbon σ-bonds in, e.g., homocubane.[23a] The region in homocubane that is predicted on the basis of these calculations to be most reactive toward electrophiles is that which is associated with the C(4)–C(7) bond.[23b] In accord with this prediction is the observation[24] that Ag(I)-promoted rearrangement of homocubane proceeds with initial rupture of the C(4)–C(7) bond, ultimately affording norsnoutane (**40**, Scheme 7).

Complexes of Rh(I) ($4d^8$) and of Pd(II) ($4d^8$) also are capable of inserting into strained carbon–carbon σ-

SCHEME 8



bonds.[25] Reactions of homocubanes with Rh(I) proceed in stepwise fashion via organorhodium intermediates (e.g., 41) that result via an oxidative addition process. Once again, initial attack of the electrophile is at the C(4)–C(7) σ-bond in the homocubane. The product, 42, that is isolated from this reaction results via cleavage of the C(4)–C(7) and C(5)–C(6) σ-bonds in the substrate (Scheme 8).[24d,25] Substituent effects on the course of Rh(I)- and Pd(II)-promoted rearrangements of homocubanes have been studied.[24d]

Hydrogenolysis of homocubanes in the presence of Pd, Pt, and Rh catalysts results in the formation of two isomeric dihydro compounds (C_9H_{12}), 43 and 44. Of these two dihydro compounds, only one, 44, reacts further to afford a tetrahydro compound, i.e., "twistbrendane" (45). In addition, the hydrogenation catalyst also promotes rearrangement of homocubane, thereby affording norsnoutane (40). Subsequently, 40 suffers hydrogenolysis to afford brendane (46). The various reactions and hydrogenolysis products are summarized in Scheme 9.[26]

In addition to the hydrogenolysis experiments described above, cleavage of strained carbon–carbon σ-bonds with concomitant fragmentation of the homocubane cage skeleton can occur under a variety of experimental conditions. Thus, homocubanone (34), a nonenolizable ketone, can be cleaved readily under basic conditions,[27] thereby affording a mixture of epimeric secocubanecarboxylic acids (47 and 48, Scheme 10).[6a]

Fragmentation of the homocubane skeleton has been carried out via base-promoted homoketonization[28] of bridgehead-substituted homocubanes. Some typical examples of this rection in appropriately substituted homocubanes are shown in Table 5.

Some features of the reactions shown in Table 5 merit comment. Homoketonization of homocubanes results in opening of the cage system with complete retention of configuration; i.e., protonation occurs exclusively at the endo face of the electrofugal carbon atom that is generated during base-promoted homoketonization.[11,29] This conclusion is supported by the results of deuterium-labeling experiments (i.e., identification of products formed via homoketonization performed in the presence of NaOMe–MeOD).[28-30] Generally, these homoketonization reactions proceed regiospecifically in cases where more than one fragmentation pathway is possible. In such instances, the thermodynamically most stable product is formed (e.g., 49 → 50, Scheme 11).[29] Exceptional in this regard is the base-promoted rearrangement of 51 to 52, which appears to be directed by the 5-bromo substituent (Scheme 12).[11]

Interestingly, different results were obtained when base-promoted homoketonization of 49 was performed by using lithium diisopropylamide as base (i.e., under aprotic conditions). Under these conditions, the anion formed via initial homoketonization appears to suffer further fragmentation, thereby affording 53. A possible mechanism for the transformation of 49 to 53 is shown in Scheme 13.[29b]

A closely related homoallylic rearrangement reaction is depicted in Scheme 14.[31] Compound **54a**, when treated with lithium diisopropylamide followed by aqueous workup, afforded an intractable mixture of ring-fragmented products (**55a** + **56a**) in essentially quantitative yield.[31] In contrast to this result, similar treatment of **54b** afforded **55b** in nearly quantitative yield; only traces of **56b** were formed in this reaction.[31]

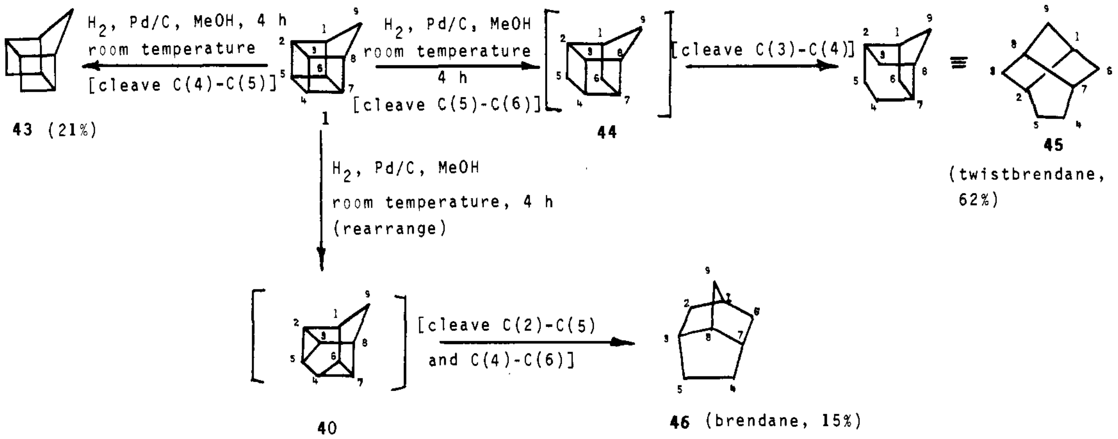
C. Cationic Rearrangements in the Homocubyl Ring System

The 9-homocubyl carbocation is of conceptual interest as a potentially fluxional species which, in principle, can achieve ninefold positional degeneracy via operation of a series of sequential Wagner–Meerwein (1,2-carbon–carbon) shifts (Figure 1). In practice, the anticipated degeneracy can be achieved simply via solvolysis of 9-substituted homocubanes.[5,12] That the 9-carbocation thereby generated is indeed degenerate was demonstrated via the observation (by nuclear magnetic resonance spectroscopy) of positional scrambling that accompanied acetolysis of 9-homocubyl tosylate-*9-d*.[5]

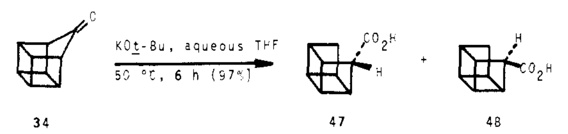
The 4-homocubyl carbocation has been generated under solvolytic conditions from the corresponding 4-Br derivative or via nitrous acid deamination of 4-aminohomocubane. Nonclassical stabilization of the 4-homocubyl carbocation has been postulated.[32]

The 9-homocubylcarbinyl carbocation has been generated via solvolysis of 9-homocubylcarbinyl tosylate

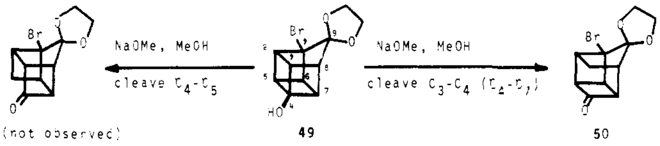
SCHEME 9



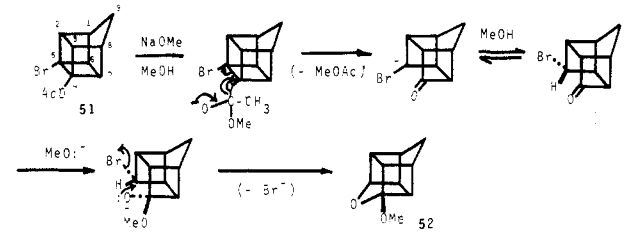
SCHEME 10



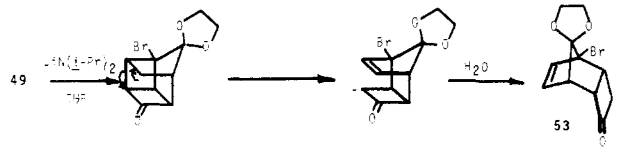
SCHEME 11



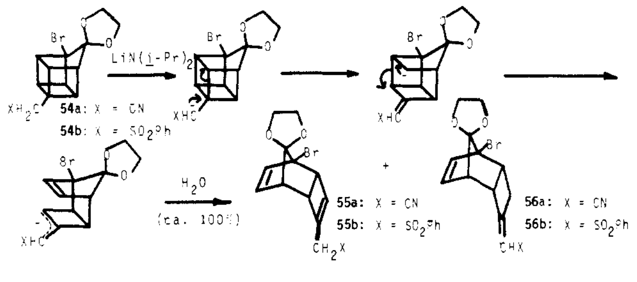
SCHEME 12



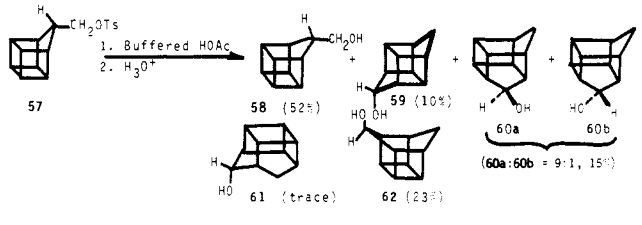
SCHEME 13



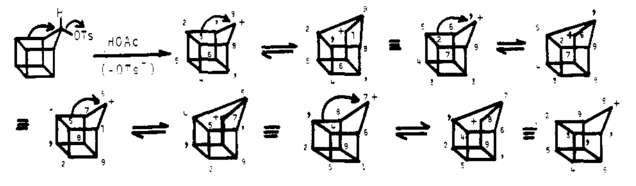
SCHEME 14



SCHEME 15



(a) Solvolysis of 9-homocubyl tosylate with stereospecific participation of the C_1–C_2 (C_3–C_8) bond results in equilibration of five positions:



(b) Nonstereospecific solvolysis permits eventual equilibration of all nine positions:

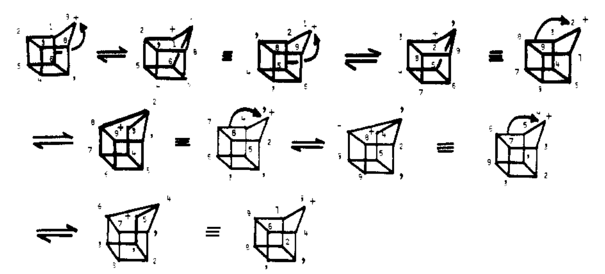
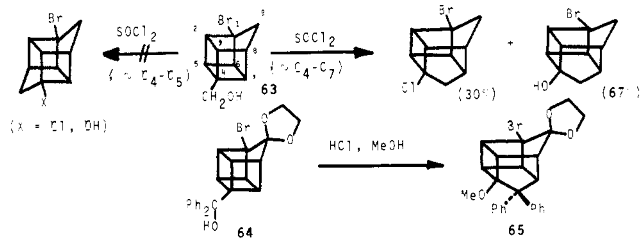
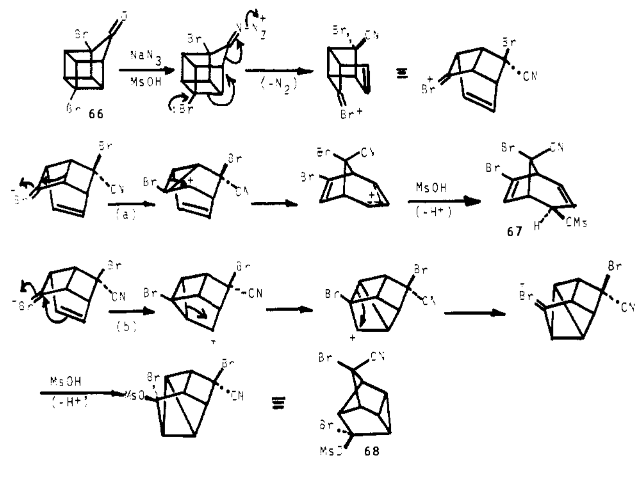


Figure 1. Wagner–Meerwein rearrangement in the 9-homocubyl carbocation.

SCHEME 16



SCHEME 17

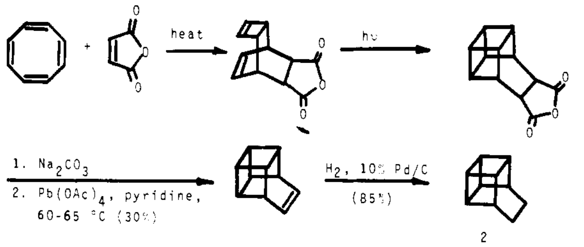


(57). The alcohols derived via hydrolysis of the mixture of cage acetates produced via acetolysis of **57** (i.e., compounds **59**–**62**) appear in Scheme 15.[33] A large number of potential rearrangement pathways are available to the 9-homocubylcarbinyl carbocation through which strain energy contained in the homocubyl ring system can be at least partially alleviated. Of particular interest is the small amount of **59** found among the solvolysis products. Formation of the corresponding acetoxy-1,4-bishomocubane via the 9-homocubylcarbinyl carbocation requires four successive Wagner–Meerwein 1,2-carbon–carbon bond migrations.[33]

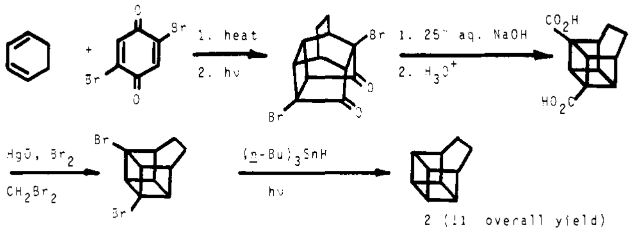
Wagner–Meerwein rearrangement has been observed to accompany the reaction of 1-bromo-4-(hydroxymethyl)homocubane (**63**) with $SOCl_2$ or with PBr_3.[34] The product is formed regiospecifically with exclusive migration of the C(3)–C(4) [or C(4)–C(7)] bond in **63**. Analogous behavior has been observed during Wagner–Meerwein rearrangement that accompanies solvolysis of **64**.[35] The structure of the solvolysis product (i.e., **65**, Scheme 16) was established unequivocally via single-crystal X-ray structural analysis.

Deep-seated cationic skeletal rearrangements in homocubanes have been observed. An example in this regard is provided by the reaction of 1,4-dibromohomocubanone (**66**) with sodium azide in methanesulfonic acid. Two products, **67** and **68** (ratio 5:1, 75% yield), were thereby obtained. Mechanistic rationalization of their formation is provided in Scheme 17.[36]

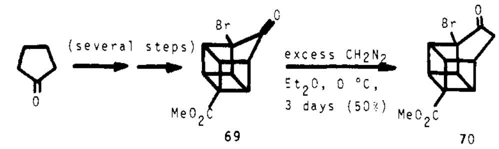
SCHEME 18



SCHEME 19



SCHEME 20



III. Bishomocubanes

A. 1,8(or 1,1′)-Bishomocubane [Basketane (2)]

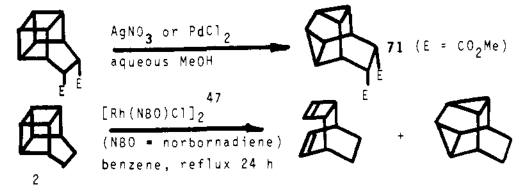
The first syntheses of 2 were reported independently in 1966 by Masamune and co-workers[37a] and by Dauben and Whalen[7] (Scheme 18). Both procedures rely upon a relatively expensive starting material, cyclooctatetraene, and neither procedure lends itself to large-scale synthesis of basketane. More recently, an improved synthesis of 2 has been reported by Gassman and Yamaguchi.[38] Their procedure affords 2 in 11% overall yield in six steps starting with the Diels–Alder addition of 1,3-cyclohexadiene to 2,5-dibromo-p-benzoquinone (Scheme 19).

Substituted basketanes have been synthesized via regiospecific one-carbon homologation of 4-substituted homocubanones (Scheme 20).[39] Most likely, the regiospecific C(8)–C(9) bond migration in **69** is controlled by the presence of the bromine substituent at C(1). It has been reported that when α-halo ketones are employed as substrates in such ketone homologation reactions, the presence of the halogen atom effectively suppresses migration of the terminus to which it is attached.

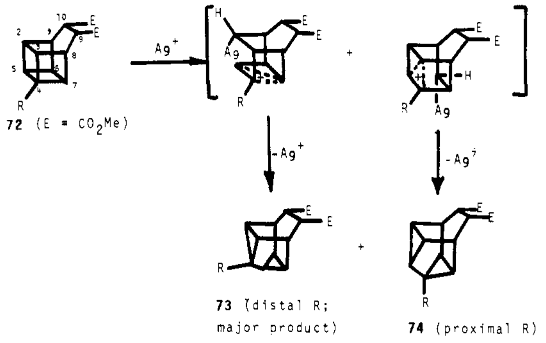
Electrophilic attack on the basketane ring system by Ag(I) catalysts[3,24c,43-46] results in the formation of snoutanes (e.g., **71**, Scheme 21), whereas similar treatment of basketanes with Pd(II),[45,47] Rh(I),[45,47] or Ni(0)[48] catalysts affords both snoutanes and ring-opened products that result via a formal [2 + 2] cycloreversion process (Scheme 21). In the case of Pd(II) and Rh(I) catalysis, both the nature of the ligand and the pattern of substitution at the C(4) and/or C(5) positions in basketane were found to have a dramatic effect upon the course of the reaction.[24c,45,47]

Silver ion promoted valence isomerization of 4-substituted basketane 9,10-diesters can, in theory, undergo four different rearrangements that lead to two isomeric, substituted snoutane diesters. It has been reported that Ag(I)-promoted valence isomerization of **72** proceeds quantitatively to afford both isomeric snoutanes, **73** and **74**. In general, the major reaction product is **73** (the distal isomer).[44b,46a] The course of this reaction has been rationalized in terms of initial attack by the electrophile at the less substituted edge bonds in the substrate [i.e., C(2)–C(5) and C(5)–C(6) (Scheme 22].[24c,44b]

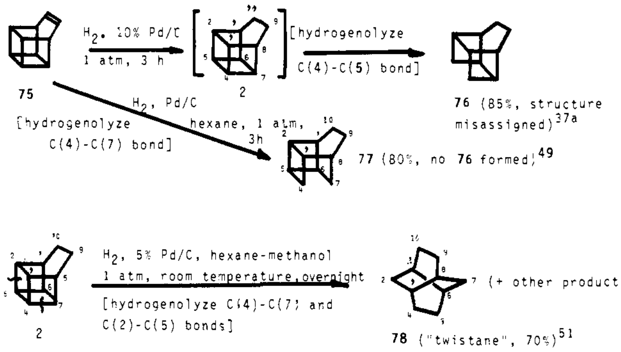
SCHEME 21



SCHEME 22



SCHEME 23



Hydrogenolysis of basketane and substituted basketanes has been studied extensively.[37a,49-51] In an early study,[37a] hydrogenation of basketene (**75**) at atmospheric pressure and ambient temperature produced a "dihydrobasketane" (**76**, 85% yield), which was believed to result via hydrogenolysis of the C(4)–C(5) bond in the presumed intermediate, basketane (**2**). This conclusion was challenged subsequently by Musso and co-workers,[49,50a] who showed that hydrogenolysis of **2** proceeds with rupture of the C(3)–C(4) bond (or other bonds in **2** that are equivalent to the C(3)–C(4) bond by symmetry) to afford an unsymmetrical product, **77**. A small amount of a "tetrahydrobasketane" was formed during hydrogenolysis of **2** at atmospheric pressure.[49,50a] It was later demonstrated[52] that reaction of **2** with hydrogen over 5% palladized charcoal in a Parr shaker (initial hydrogen pressure 3.3 atm) at room temperature affords twistane (**78**) in 70% yield along with at least three other minor products. These reactions are summarized in Scheme 23.

The results of force field calculations[52] confirm that, of the seven possible modes of hydrogenolytic ring

TABLE 1. Listing of Homocubanes, Bishomocubanes, and Trishomocubanes

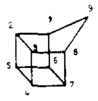
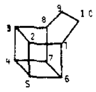
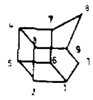
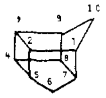
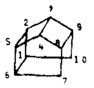
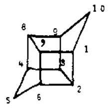
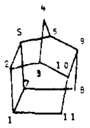
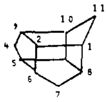
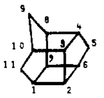
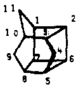
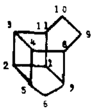
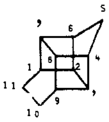
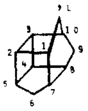
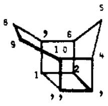
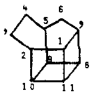
structure	name(s)	registry no.
I. homocubane (C_9H_{10})		
 1	pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane homocubane	452-61-9
II. bishomocubanes ($C_{10}H_{12}$)		
 2	pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane 1,1′-bishomocubane; 1,8-bishomocubane; basketane	5603-27-0
 3	pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,7}]decane 1,2-bishomocubane	
 4	pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene C_2-bishomocubane; 1,3-bishomocubane	6707-86-4
 5	pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane C_{2v}-bishomocubane; secopentaprismane	7172-92-1
 6	pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane octahydro-1,3,4-metheno-1*H*-cyclobuta[*cd*]pentalene D_{2h}-bishomocubane	6707-88-6
III. trishomocubanes ($C_{11}H_{14}$)		
 7	pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane octahydro-1,2,4-ethanylylidene-1*H*-cyclobuta[*cd*]pentalene	4421-32-3
 8	pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane decahydro-1,3,5-methenocyclopenta[*cd*]pentalene D_3-trishomocubane	30144-56-8
 9	pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane decahydro-1,3,6-methenocyclopenta[*cd*]pentalene	63231-04-9
 10	pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecane octahydro-4,1,2-ethanylylidene-1*H*-cyclobuta[*cd*]pentalene	63231-09-4
 11	pentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,8}]undecane decahydro-1,2,4-methenocyclobut[*cd*]indene 1,3-ethanomethanocubane; C_1-homobasketane [2.1.0]triblattane	62415-12-7
 12	pentacyclo[5.4.0.0^{2,6}.0^{3,9}.0^{4,8}]undecane decahydro-1,3,4-methenocyclobut[*cd*]indene C_{2v}-homobasketane	63231-12-9
 13	pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane octahydro-2,1,4-ethanylylidene-1*H*-cyclobuta[*cd*]pentalene	63231-03-8
 14	pentacyclo[5.4.0.0^{2,6}.0^{3,11}.0^{4,10}]undecane C_s-homobasketane	63231-13-0
 15	pentacyclo[5.4.0.0^{2,10}.0^{5,9}.0^{8,11}]undecane	

TABLE 1 (Continued)

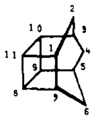
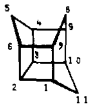
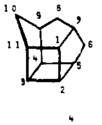
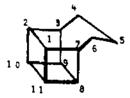
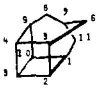
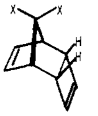
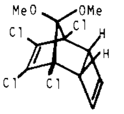
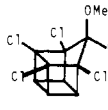
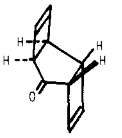
structure	name(s)	registry no.
 **16**	pentacyclo[5.4.0.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]undecane octahydro-2,1,5-ethanylylidene-1*H*-cyclobuta[*cd*]pentalene	63231-08-3
 **17**	pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,9}$]undecane decahydro-1,3-methanodicyclobuta[*cd*,*gh*]pentalene	63231-10-7
 **18**	pentacyclo[5.4.0.$0^{2,5}$.$0^{3,11}$.$0^{4,9}$]undecane decahydro-1,2,5-methenocyclobut[*cd*]indene	63231-11-8
 **19**	pentacyclo[5.4.0.$0^{2,10}$.$0^{3,9}$.$0^{8,11}$]undecane	61304-39-0
 **20**	pentacyclo[5.3.1.$0^{2,5}$.$0^{3,10}$.$0^{4,9}$]undecane	63451-58-1

TABLE 2. Syntheses of Homocubanes via Intramolecular [2 + 2] Photocycloaddition Reactions

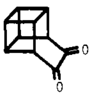
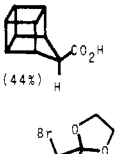
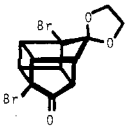
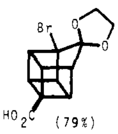
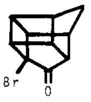
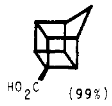
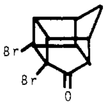
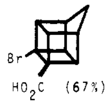
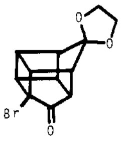
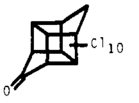
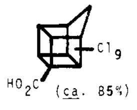
reactant	conditions	product (% yield)	ref
	X = H or OEt, *hν*, sens	 1 (X = H) (X = OEt)	3 (X = H) 5 (X = OEt)
	*hν*, Vycor filter, room temp, 4 h	 (96%)	6
	*hν*, Corex filter, CH_2Cl_2, 3.5 h	 **34** (68%)	4

opening of **2** that might afford "tetrahydrobasketanes", that which results in the formation of **78** is predicted to proceed with the most negative heat of hydrogenation and the greatest net relief of strain. Thus, the prediction that **78** should be the major product of this reaction concurs with experiment.[50b]

Homoketonization of 4-substituted basketanes has been studied by Zwanenburg and co-workers.[53] 1-Bromo-4-acetoxybasketan-10-one (**79a**) and its corresponding ethylene and dithioethylene ketals (**79b** and **79c**, respectively), when treated briefly with methanolic sodium methoxide, undergo regio- and stereospecific ring opening to afford substituted secobasketanes **80a–c**, respectively, with exclusive C(4)–C(7) σ-bond cleavage. Prolonged treatment of **79b** or of **79c** with base instead resulted in further ring fragmentation, thereby affording substituted bicyclo[2.2.2]octanes (i.e., **81** or **82**, respectively). Treatment of either **80a** or **80b** with methanolic HCl resulted in the formation of a substituted homobrendanedione (**83**). These reactions are summarized in Scheme 24.[53]

Cationic skeletal rearrangements have been observed in the basketane system. Thus, treatment of pentacy-

TABLE 3. Syntheses of Homocubanes via Ring Contraction of Substituted Bishomocubanes

reactant	conditions	product (% yield)	ref
	1. $TsNHNH_2$ 2. aq NaOH 3. *hν*, Corex filter, THF	 (44%)	7
	1. aq KOH, heat 2. acidify	 (79%)	8
	1. 30% aq KOH, reflux 4 h 2. dil aq HCl	 (99%)	9, 10
	1. 30% aq KOH, 100–110 °C, 1.5 h 2. 30% aq HCl	 (67%)	11
	1. 10% aq KOH (62%) 2. HgO-Br_2 (51%) 3. Li, *t*-BuOH (57%) 4. H_2SO_4	 (85%)	12
	1. 85% KOH pellets, refluxing xylene 2. acidify	 (ca. 85%)	13

SCHEME 24

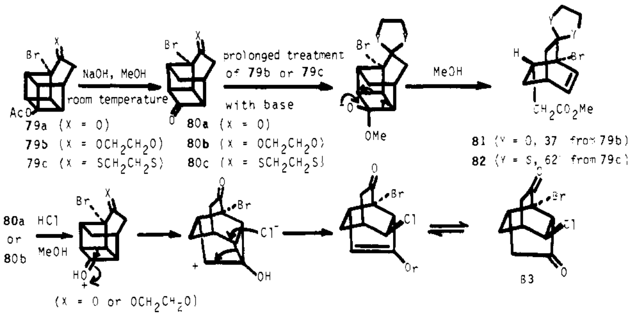


TABLE 4. Base-Promoted Ring Fragmentation Reactions in Cage α-Halo Ketones

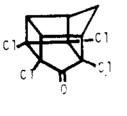
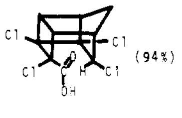
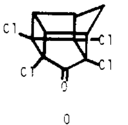
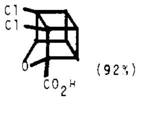
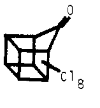
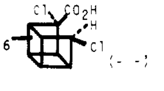
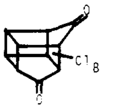
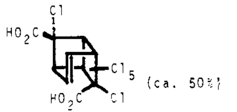
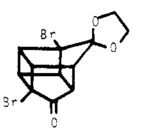
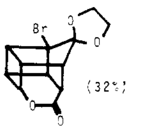
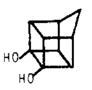
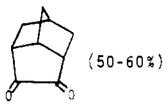
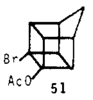
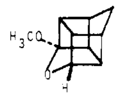
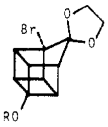
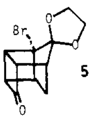
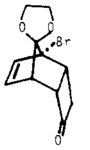
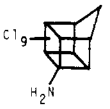
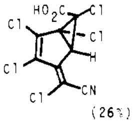
reactant	conditions	product (% yield)	ref
	30% aq KOH, dioxane, reflux 4 h *or* NaOH, benzene, reflux 21 h	 (94%)	6a, 9b
	30% aq KOH, reflux 6 h under N_2	 (92%)	6a
	10% aq KOH, reflux	 (- -)	13
	10% aq KOH, reflux	 (ca. 50%)	13
	KOH, aq DMSO, room temp, stir overnight	 (32%)	8

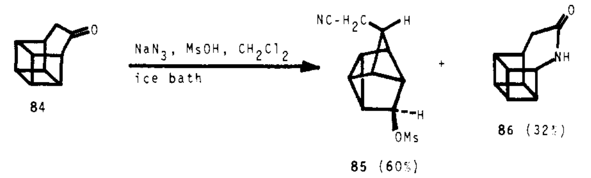
TABLE 5. Base-Induced Homoketonization of Bridgehead-Substituted Homocubanes

substrate	conditions	product (% yield)	ref
	0.5 M methanolic NaOMe (2 equiv), 25 °C	 (50-60%)	30
 51	NaOMe, MeOH, room temp, stir 1 h; quench via addition of NH_4Cl	 52 (37%)	11
 49 (R = H, Ac)	NaOMe, MeOH, room temp, stir 1 h	 50 (ca. 100%)	29
49 (R = H, Ac)	*n*-BuLi, HN(*i*-Pr)$_2$, hexane–THF, room temp, stir 1 h	 53 (58%)	29
	0.08 N KOH, aqueous *t*-BuOH, room temp, 10 min	 (26%)	31

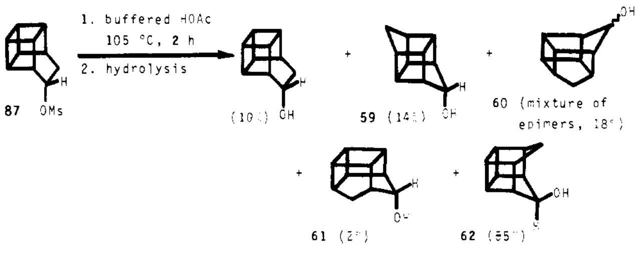
clo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-one ("basketanone" (84)) with sodium azide–methanesulfonic acid results in the formation of 4-(cyanomethyl)-7-(mesyloxy)tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (85, 60% yield) and 4-aza-5-oxopentacyclo[5.4.0.0^{2,10}.0^{3,9}.0^{8,11}]undecane (86, 32% yield) (Scheme 25).[54]

Solvolytic reactions of appropriately substituted basketanes have been studied. Thus, acetolysis of mesylate 87 followed by hydrolysis of the resulting mixture of acetates afforded alcohols that possess all five possible bishomocubyl carbon frameworks (Scheme 26).[33] A series of consecutive carbonium ion rearrangements was suggested to account for the course of this reaction.[33]

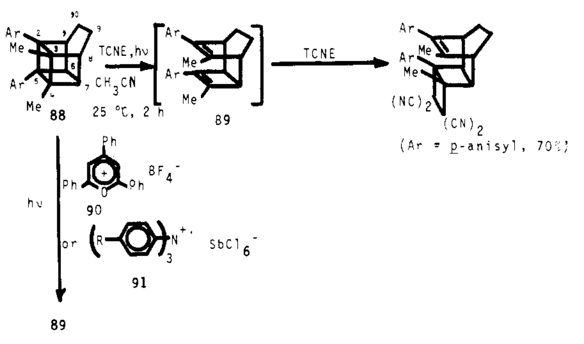
SCHEME 25



SCHEME 26



SCHEME 27

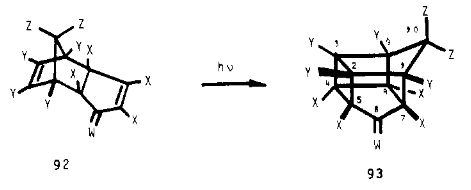


Valence isomerizations of 2,5-diaryl-3,4-dimethylbasketanes (88) have been studied as a model system for solar energy storage.[55] When benzene solutions of these substituted basketanes are heated to reflux, thermal [2 + 2] cycloreversion occurs, thereby affording the corresponding dienes (89). Subsequent studies have shown that cycloreversion of 88 to 89 can be performed photochemically in the presence of ZnO or CdS or thermally in the presence of ceric ammonium nitrate.[56] Additionally, it was found that this cycloreversion reaction can be promoted by photoexcitation of the charge-transfer complex that is formed when compounds of the type 88 are reacted with tetracyanoethylene (TCNE) in acetonitrile solution.[56,57] Photocycloreversion of 88 to 89 also can be catalyzed by addition of pyrilium salt 90[58] or by addition of triarylaminium cation radical salts (e.g., 91,[59] Scheme 27). An electron-transfer radical cation chain mechanism was suggested to account for the catalyzed cycloreversion reactions.[56-60]

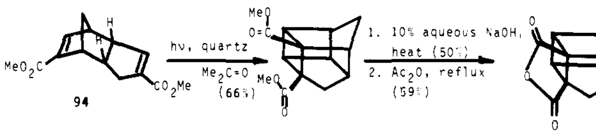
B. 1,2-Bishomocubane (3)

A search of the literature reveals only one example that resulted in the synthesis of a substituted 1,2-bishomocubane. Thus, acetolysis of either 9-homocubylmethyl tosylate (57, Scheme 15, section II.C) or of basketane mesylate 87 (Scheme 26, section III.A) followed in each case by hydrolysis of the mixture of cage acetates thereby obtained afforded 8-hydroxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,7}]decane (61) in low yield along with several other cage alcohols.[33]

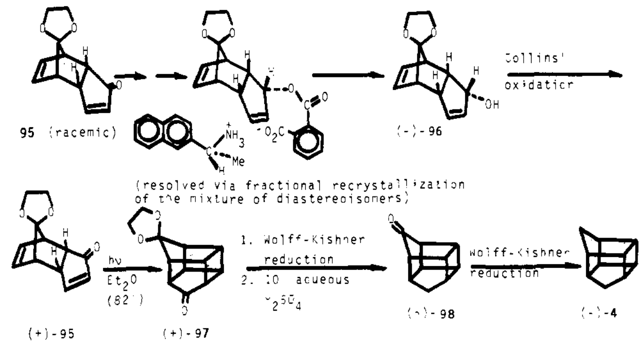
SCHEME 28



SCHEME 29



SCHEME 30



C. 1,3-Bishomocubane (4)

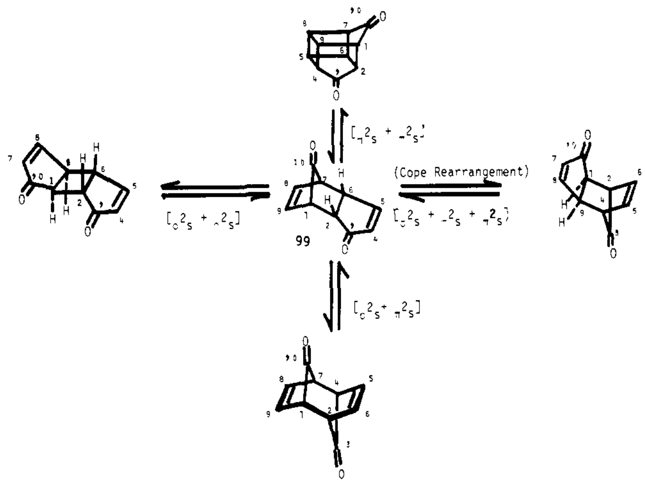
Substituted 1,3-bishomocubanes (**93**) can be prepared readily via [2 + 2] photocyclization of the corresponding substituted *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dienes (**92**, Scheme 28).[61,62]

This approach appears to offer the best general route for synthesizing substituted 1,3-bishomocubanes. In an interesting application of this reaction in substituted *endo*-dicyclopentadienes, intramolecular [2 + 2] photocyclization has been utilized to establish unequivocally the structure of Thiele's ester[63] (**94**, Scheme 29).[64]

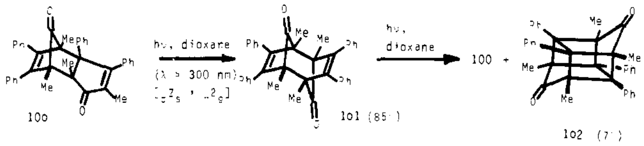
1,3-Bishomocubane, which possesses C_2 symmetry, is the only one of the five bishomocubane isomers listed in Table 1 that is chiral. Syntheses of optically active 1,3-bishomocubanes have been reported by Nakazaki and co-workers (Scheme 30).[65-67] The absolute configuration and absolute rotation of (−)-(1*S*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*)-1,3-bishomocubane have been determined.[65,66]

endo-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dienes (i.e., *endo*-cyclopentadiene dimers) generally undergo smooth intramolecular [2 + 2] photocyclization to afford the corresponding, substituted 1,3-bishomocubanes, as noted above.[61] By way of contrast, the corresponding photochemical behavior of substituted *endo*-cyclopentadienone dimers has been found to be significantly more complicated.[68-75] Thus, irradiation of *endo*-cyclopentadienone dimer (**99**) affords products that correspond to all possible modes of molecular interconversion (Scheme 31).[71] All of the interconversions shown in Scheme 31 with the exception of the Cope rearrangement are photochemically "allowed" processes, if concerted.[76] An additional example in this regard is provided by the photochemical behavior of the Diels–Alder dimer of 1,4-dimethyl-2,3-diphenylcyclopentadienone (**100**, Scheme 32). The mechanisms of photochemical transformation of reversibly dissociating and of nondissociating cyclopentadienone dimers (e.g., **100**[74] and **99**,[71] respectively) have been studied extensively by Fuchs and co-workers. The reader is referred to the appropriate primary literature for further discussion of this subject.[68-71,73-75]

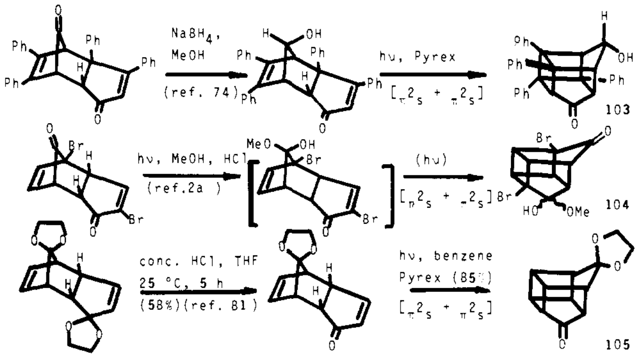
SCHEME 31



SCHEME 32

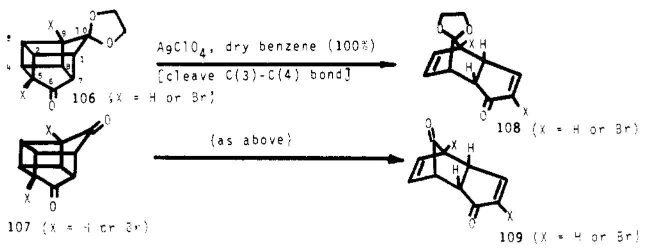


SCHEME 33

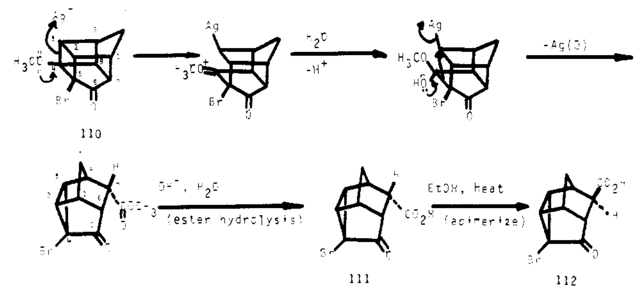


Substituted *endo*-cyclopentadienone dimers can be used as precursors for the synthesis of the corresponding substituted 1,3-bishomocubanes provided that the hybridization of C(10) in the substrate is sp^3 (rather than sp^2, as it would otherwise be in a cyclopentadienone dimer). This can be accomplished in any of a number of ways: e.g., (i) by selective reduction of the (nonconjugated) C(10) carbonyl group with sodium borohydride,[72,77] (ii) by selective hemiketal formation at C(10),[2a] or (iii) by selective hydrolysis of the ethylene ketal functionality at C(3) in a substituted *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione bis(ethylene ketal).[78-80] An example of the application of each of these reactions to the synthesis of a substituted 1,3-bishomocubane (**103–105**, respectively) is shown in Scheme 33. 1,3-Bishomocubanes also have been synthesized via solvolytic ring expansion of appropriately substituted homocubylcarbinols. This topic has been discussed earlier in this review (cf. Scheme 16 and discussion in section II.C).

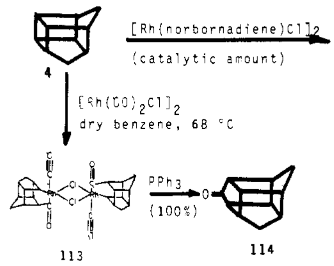
SCHEME 34



SCHEME 35



SCHEME 36



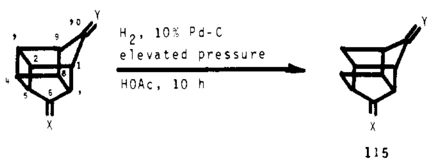
Electrophilic attack on substituted 1,3-bishomocubanones (**106**) and 1,3-bishomocubanediones (**107**) by Ag(I) results in the formation of the corresponding substituted *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dienes (**108** and **109**, respectively, Scheme 34).[81] The products, **108** and **109**, are those that result via initial attack of Ag$^+$ on the most highly strained σ-bond [i.e., the C(3)–C(4) bond] in the substrates.

A different result was obtained when a suspension of **110** in 20% aqueous potassium hydroxide was treated with excess silver nitrate at 60 °C. Workup of the reaction mixture afforded a single carboxylic acid, 5-oxo-4-bromotetracyclo[4.3.0.0^{2,4}.0^{3,8}]nonane-*endo*-7-carboxylic acid (**111**, 85% yield). Repeated recrystallization of **111** from ethanol resulted in epimerization at C(7), thereby converting **111** into the corresponding *exo*-7-carboxylic acid (**112**). A mechanism that accounts for the formation of **111** and **112** in this reaction is presented in Scheme 35.[11,82] As in the case of the corresponding reactions of **106** and **107** with Ag$^+$ (Scheme 34), the reaction of Ag$^+$ with **110** is initiated by regiospecific attack of the electrophile on the C(3)–C(4) σ-bond in the substrate.

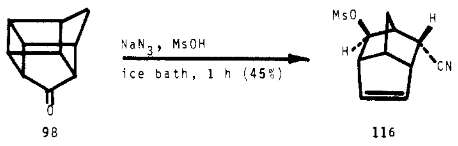
The behavior of Rh(I) complexes toward 1,3-bishomocubanes differs significantly from that of Ag(I). Whereas [Rh(norbornadiene)Cl]$_2$ reacts with **4** to afford *endo*-dicyclopentadiene, [Rh(CO)$_2$Cl]$_2$ instead reacts with **4** to afford a dinuclear acylrhodium complex, **113**, that can be transformed subsequently into *endo*-dicyclopentadiene or into a trishomocubanone (**114**, Scheme 36).[83]

Hydrogenolysis of 1,3-bishomocubane has been studied by Hirao and co-workers.[84,85] As was found to

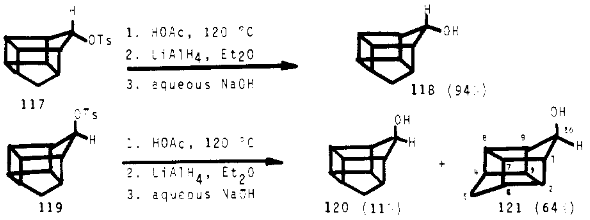
SCHEME 37



SCHEME 38



SCHEME 39



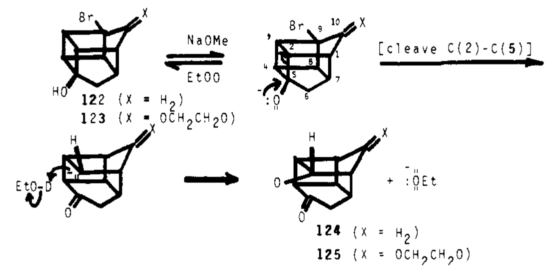
be the case for attack by Rh(I) on substituted 1,3-bishomocubanes, bond cleavage occurs preferentially at the C(3)–C(4) σ-bond. These results are consistent with predictions based upon the results of empirical force field calculations.[29c,86] This hydrogenolysis reaction has been used to synthesize substituted tetracyclo-[5.2.1.0^{2,6}.0^{4,8}]decanes ["bisnorditwistanes" (**115**)] from the corresponding, substituted 1,3-bishomocubanes (Scheme 37).[84,85,87,88]

Sodium azide–methanesulfonic acid promoted cationic skeletal rearrangement of 1,3-bishomocubanone (**98**) has been studied. This reaction is analogous to corresponding reactions of homocubanone and of "basketanone" that have been discussed earlier (cf. Schemes 17[36] and 25,[54] respectively). Thus, treatment of **98** with sodium azide–methanesulfonic acid resulted in the formation of *exo*-2-(methylsulfonyl)-9-cyanobrend-4-ene (**116**) in 45% yield (Scheme 38).[89]

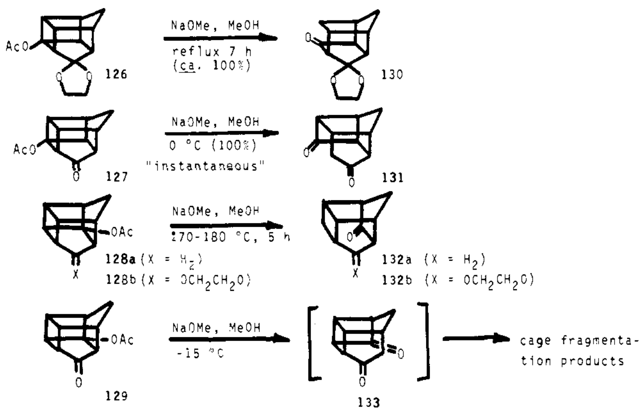
Solvolytic reactions of appropriately substituted 1,3-bishomocubanes have been studied. Whereas acetolysis of *syn*-10-(tosyloxy)-1,3-bishomocubane (**117**) affords (after reduction with lithium aluminum hydride) nearly exclusively the corresponding unrearranged *syn*-10 alcohol (**118**), acetolysis of *anti*-10-(tosyloxy)-1,3-bishomocubane (**119**) affords a mixture of the unrearranged *anti*-10-hydroxy-1,3-bishomocubane (**120**, 11%) together with the symmetrical, rearranged pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-10-ol (**121**, 64%; see Scheme 39).[90,91] These results have been rationalized in terms of bridged ("nonclassical") carbocationic intermediates (cf. Figure 1 and discussion in section II.C) and in terms of unimolecular nucleophilic substitution that proceeds with retention of configuration.[91,92]

Base-promoted ring fragmentations in appropriately substituted 1,3-bishomocubanes have been studied extensively by Zwanenburg and co-workers.[11,28,29b,92,93] As in the case of the corresponding fragmentation processes in homocubanes and in basketanes, ring opening occurs with complete retention of configuration.[11,28] A mechanism that accounts for the observed mode of NaOMe–EtOD-promoted fragmentation of 5-hydroxy-9-bromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanes **122** and **123**

SCHEME 40



SCHEME 41



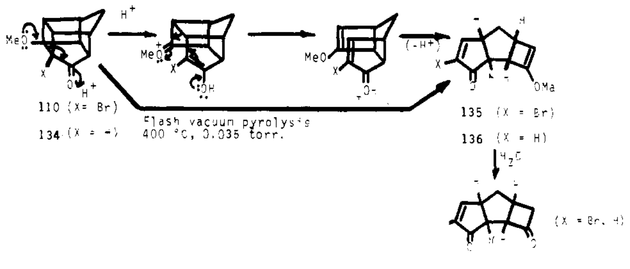
(which afford **124** and **125**, respectively) is shown in Scheme 40.[29b]

The regiochemistry of base-promoted homoketonization of substituted 4- and 8-acetoxy-1,3-bishomocubanes has been found to be influenced strongly by β-substituents as illustrated by the examples shown in Scheme 41.[92,93] In **126** and **128** the 6-substituent (hydrogen or OCH$_2$CH$_2$O) is incapable of stabilizing a carbanionic intermediate and/or transition state. It has been suggested[29c] that the observed cage fragmentation products (**130** and **132**, respectively) are those that would be expected to result simply via (thermodynamically controlled) cleavage of the C(3)–C(4) σ-bond in the reactants. However, in the case of **127** and **129**, the C(6) carbonyl substituent, which is capable of conjugative stabilization of a carbanionic transition state, might be expected to promote (contrathermodynamic) scission of the C(4)–C(5) σ-bond in each of the reactants.[92] The results of empirical force field calculations provide additional theoretical insight that supports these suggestions.[29c,93]

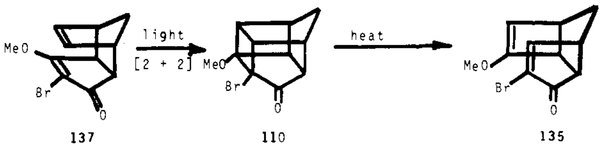
Thermal ring opening of 4-methoxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ones **110** and **134** has been studied by using flash vacuum pyrolysis techniques. Thus, when **110** and **134** were heated in the gas phase at 400 °C/0.035 Torr, cleavage of a cyclobutane ring in both **110** and **134** occurred, thereby affording the corresponding dienes (**135** and **136**, respectively).[11,82] Cage opening of **110** and **134** could also be accomplished by treating a toluene solution of either substrate with hydrogen chloride gas. A summary of these reactions and a mechanism for the acid-catalyzed ring opening of **110** and **134** are shown in Scheme 42.[11,82]

Compound **110** was synthesized by intramolecular [2 + 2] photocyclization of 4-bromo-5-methoxy-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**137**).[11,82] The overall reaction sequence, **137** → **110** → **135**, is an example of "photothermal metathesis" (Scheme 43).[94,95] Reactions of this type have been utilized extensively for the synthesis of linearly fused cis,syn,cis tricyclic systems, in particular cis,syn,cis linear "triquinanes" and natural products that contain this ring system.[94,95]

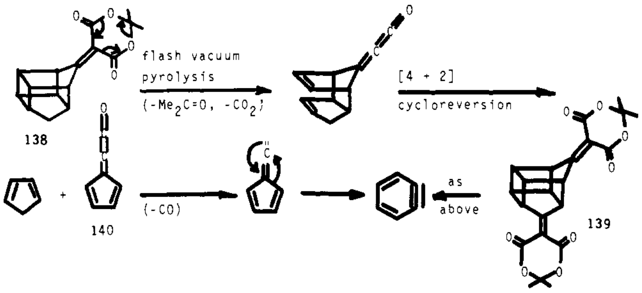
SCHEME 42



SCHEME 43



SCHEME 44

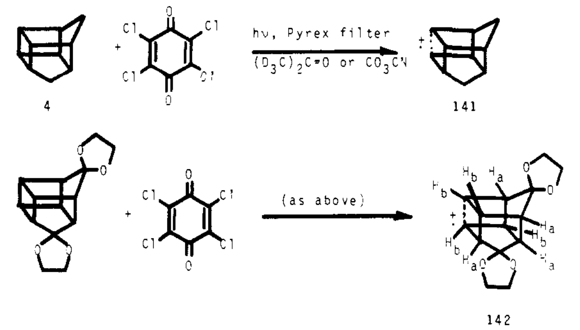


Gas-phase thermolysis of two substituted 1,3-bishomocubanes, **138** and **139**, in each case affords a vinylideneketene, **140**, which then suffers further fragmentation to benzyne.[96] Mechanistic rationalization of the fragmentation of **138** is provided in Scheme 44.[96]

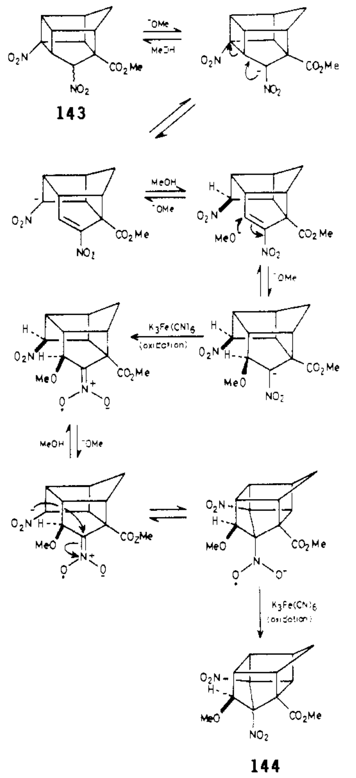
Formation of 1,3-bishomocubyl radical cations and studies of their subsequent reactions have been the subjects of recent investigations. The 1,3-bishomocubyl radical cation, **141**, has been generated by argon resonance photoionization of the parent hydrocarbon, **4**,[97] and also by γ-irradiation of **4** in freon matrices at 77 K.[98] When the species that was generated by argon resonance photoionization of **4** was photolyzed subsequently, a mixture of isomeric 1,3,5,7,9-decapentaene radical cations was produced. The formation of *all-trans*-1,3,5,7,9-decapentaene radical cation from **141** in this reaction was rationalized via a series of sigmatropic shifts and electrocyclic processes.[97] When formation of **141** instead was carried out in freon matrices, a dicyclopentadiene cation radical, $C_{10}H_{12}^{\bullet+}$, was produced.[98]

In a more recent study, Roth and co-workers[99] reacted both **4** and 1,3-bishomocubanedione bis(ethylene ketal) with photoexcited chloranil. Weak chemically induced dynamic nuclear polarization (CIDNP) effects were produced in the proton NMR spectra of the reaction products (**141** and **142**, respectively). Specifically, emission signals were noted for the methine protons, but no polarization was observed for the methylene protons in **141**. In the case of **142**, the four methine protons that are situated adjacent to the ketal moiety (i.e., H$_a$, which absorb at δ 2.85) appear in emission, while the remaining methine protons (H$_b$, which absorb

SCHEME 45



SCHEME 46[a]



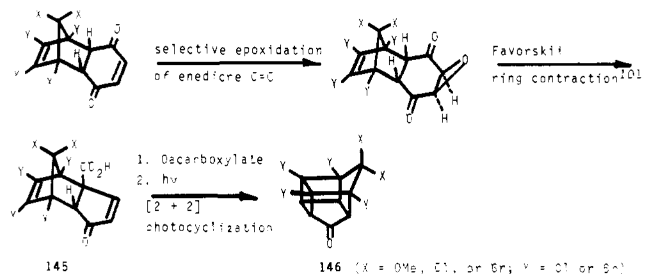
[a] Reprinted from ref 100; copyright 1987 The Royal Society of Chemistry.

at δ 2.45) display enhanced absorption. These results are summarized in Scheme 45.[99]

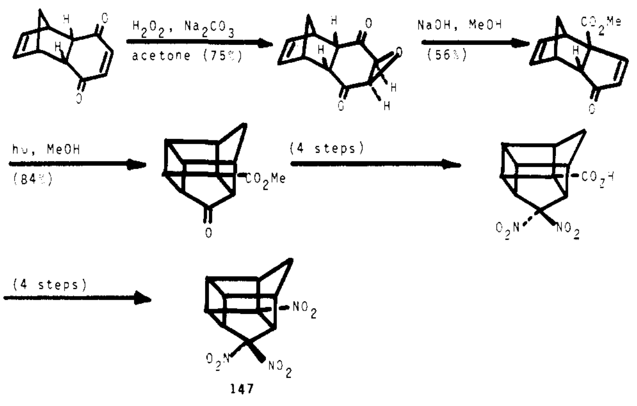
An unusual rearrangement in a substituted 1,3-bishomocubane that proceeds via an intermediate radical anion has been reported recently.[100] Thus, treatment of methyl 3,10-dinitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-8-carboxylate (**143**) with potassium ferricyanide–sodium nitrite reagent in the presence of base afforded methyl 3,9-dinitro-*exo*-10-methoxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-8-carboxylate (**144**). This reaction is unusual in that the 1,3-bishomocubyl ring skeleton is preserved in the rearrangement product. A mechanism that accounts for the course of the rearrangement of **143** to **144** is shown in Scheme 46.[100]

Functionalization of the 1,3-bishomocubane ring skeleton has been studied extensively. This is usually accomplished by placing substituents at appropriate positions in a synthetic precursor rather than by direct substitution onto the 1,3-bishomocubane ring. Such an approach was discussed previously for the example of intramolecular [2 + 2] photocyclization of substituted *endo*-cyclopentadienone dimers (cf. Scheme 33). A

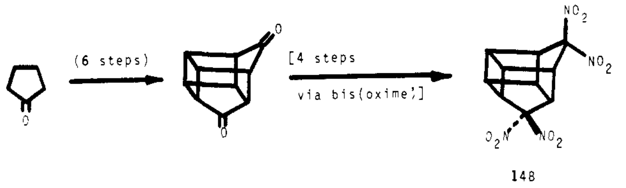
SCHEME 47



SCHEME 48



SCHEME 49

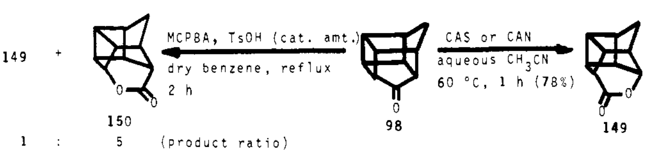


related approach is illustrated in Scheme 47; here, the key step involves the synthesis of an appropriately functionalized *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**145**)[101] which subsequently can undergo intramolecular [2 + 2] photocycloaddition to afford the corresponding, substituted 1,3-bishomocubanone, **146**. This approach has been utilized successfully to synthesize several polynitro-1,3-bishomocubanes.[77,80,102] These compounds are of interest as a potential new class of explosives and propellants.[103,104] Examples in this regard are provided by the syntheses of 6,6,8-trinitro- and 6,6,10,10-tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]decanes (**147**[102] and **148**,[80] Schemes 48 and 49, respectively).

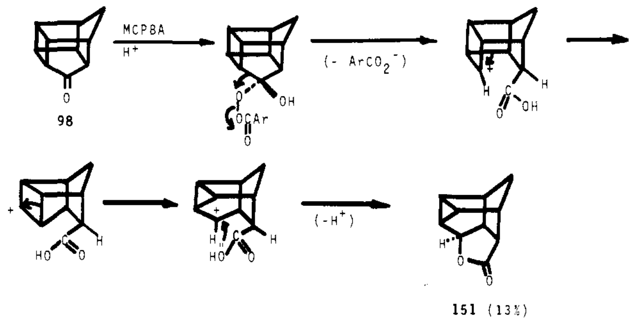
Ring expansions in the 1,3-bishomocubyl system have been promoted by reactions of substituted 1,3-bishomocubanones with Ce(IV)[105] and with *m*-chloroperbenzoic acid (Baeyer–Villiger reaction).[105,106] Carbocyclic ring expansions, which are promoted by reactions of substituted bishomocubanones with diazoalkanes,[39,42,107-109] have also been studied; these will be discussed in sections IV.E and IV.F.

Mehta and co-workers[105] reported that the reaction of 1,3-bishomocubanone (i.e., *rac*-**98**) with either ceric ammonium sulfate (CAS) or ceric ammonium nitrate (CAN) in aqueous acetonitrile proceeds regiospecifically to afford lactone **149** in 78% yield. In contrast to this result, oxidation of (*rac*) **98** with *m*-chloroperbenzoic acid in dry benzene solution in the presence of a catalytic amount of *p*-toluenesulfonic acid at room temperature for 2 h afforded two lactones, **149** and **150** (product ratio 1:5, Scheme 50).[105]

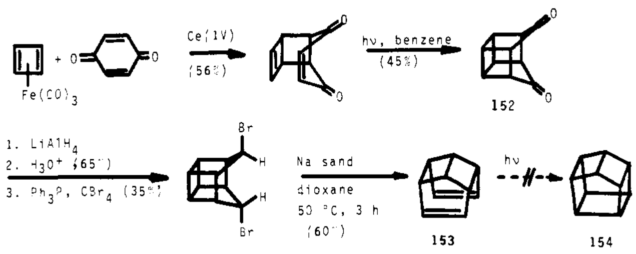
SCHEME 50



SCHEME 51



SCHEME 52



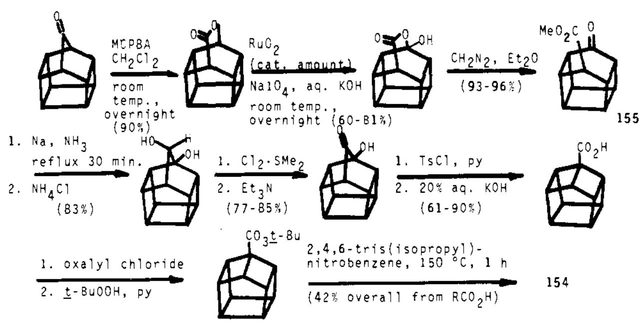
Different results were obtained by Hirao and co-workers[106] as a result of their investigation of the Baeyer–Villiger oxidation of 1,3-bishomocubanone. Thus, reaction of 1,3-bishomocubanone with a chloroform solution of *m*-chloroperbenzoic acid (1.5 equiv) at room temperature for 1 h afforded a mixture of *three* lactones: **149** (1.1%), **150** (major product, 50%), and a rearranged lactone, **151** (13%). A control experiment established that **151** is a primary reaction product and is not formed in this reaction via subsequent acid-promoted rearrangement of **150**. Furthermore, when the polarity of the solvent medium was increased, the ratio of **151** to **150** was found also to increase. A mechanism was forwarded to account for the formation of **151** in this reaction that proceeds via one or more cationic intermediates (Scheme 51).[106]

D. C_{2v}-Bishomocubane [Secopentaprismane (5)]

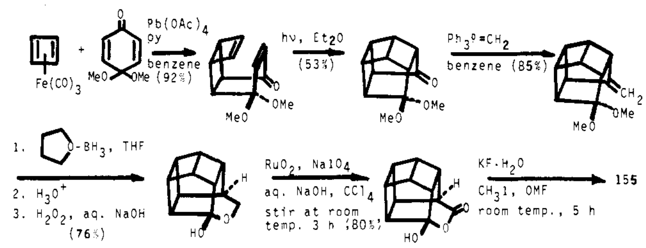
Secopentaprismane-7,10-dione (**152**) was synthesized by Pettit and co-workers.[110,111] The material thereby obtained was converted subsequently to hypostrophene (**153**, Scheme 52). At the time that it was first synthesized, hypostrophene was of intense interest as a potential precursor to pentaprismane (**154**). However, it was found subsequently that hypostrophene could not be induced to undergo the requisite [2 + 2] photocyclization to afford pentaprismane.[110–113]

More recently, a substituted secopentaprismane, **155**, served as a valuable intermediate in what proved to be the first successful synthesis of pentaprismane (Scheme 53).[114,115] Compound **155** also has been synthesized by Dauben and Cunningham in their "formal" synthesis of pentaprismane.[116] The route that they employed for this purpose is shown in Scheme 54.

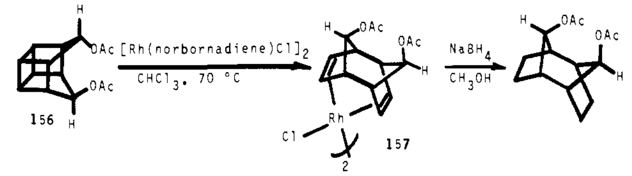
SCHEME 53



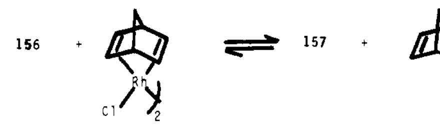
SCHEME 54



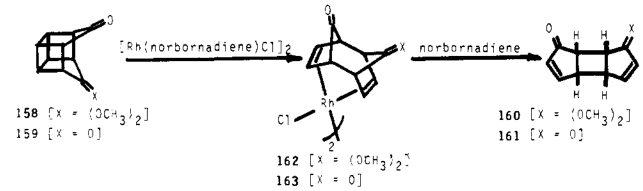
SCHEME 55



SCHEME 56



SCHEME 57

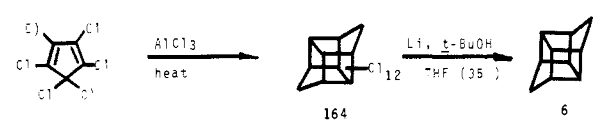


Rh(I)-promoted cleavages of secopentaprismanes have been studied by Eaton and Patterson.[117] As an example in this regard, reaction of **156** with [Rh(norbornadiene)Cl]$_2$ in chloroform at 70 °C results in ring opening to afford **157** (Scheme 55). Of particular interest is the fact that treatment of ring-opened product, **157**, with excess norbornadiene results in the establishment of a cleavage–closure equilibrium as indicated in Scheme 56.[117] In addition, Rh(I)-promoted cleavage of substituted secopentaprismanones **158** and **159** was found to result in the formation of substituted *cis,-syn,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,9-dienes (**160** and **161**, Scheme 57). Intermediate rhodium complexes, **162** and **163**, respectively, have been isolated and characterized in these reactions.

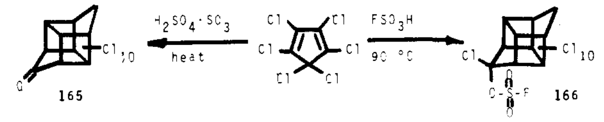
E. 1,4-Bishomocubane (6)

In 1946, Prins[118] isolated a $C_{10}Cl_{12}$ dimer, mp 485 °C, from the reaction of hexachlorocyclopentadiene with anhydrous aluminum chloride. The structure of this dimer was the subject of controversy for several years

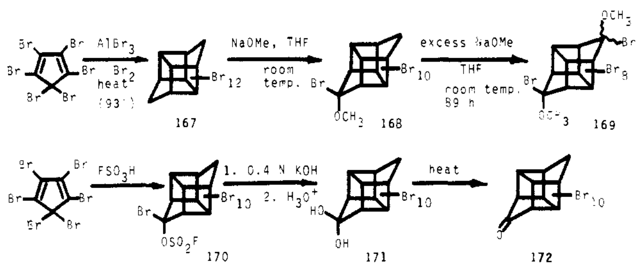
SCHEME 58



SCHEME 59



SCHEME 60



after its initial discovery. In 1956, McBee and coworkers[119] suggested cage structure **164** for this dimer.[120] It was demonstrated subsequently that reductive dehalogenation of a tetrahydrofuran solution of **164** with lithium and *tert*-butyl alcohol afforded the parent hydrocarbon, **6**, in low yield along with several partially hydrogenolyzed derivatives of this cage system (Scheme 58).[121-123]

A related cage structure, **165**, was suggested for the product, mp 350 °C, that had been reported previously to result from the corresponding reaction of hexachlorocyclopentadiene with liquid sulfur trioxide, chlorosulfonic acid, or fuming sulfuric acid (followed by hydrolysis of sulfur-containing intermediates).[120] The dimethyl ketal of **165** has been synthesized.[124] The structure of the product that is formed via the reaction of hexachlorocyclopentadiene with fluorosulfonic acid[125] was shown by single-crystal X-ray structural analysis[126] to be the corresponding undecachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane-5-fluorosulfonate, **166** (Scheme 59).

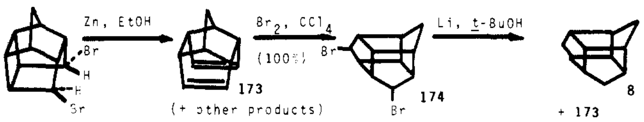
Hexabromocyclopentadiene, when refluxed in $AlBr_3$–Br_2, affords the corresponding dodecabromo-1,4-bishomocubane (**167**) in excellent yield.[127,128] Reaction of **167** with sodium methoxide in tetrahydrofuran can provide either the corresponding undecabromo-5-methoxy compound (**168**) or the corresponding decabromo-5,10-dimethoxy compound (**169**). Reaction of hexabromocyclopentadiene with excess fluorosulfonic acid afforded the corresponding undecabromo-5-fluorosulfonate (**170**). Hydrolysis of **170** with 0.4 N aqueous potassium hydroxide solution followed by aqueous acidic workup gave the corresponding ketone hydrate, **171**, which could be dehydrated by heating to afford ketone **172**.[129] These reactions are summarized in Scheme 60.

IV. Trishomocubanes

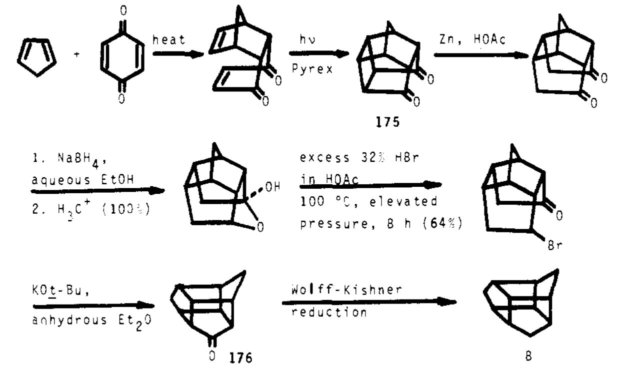
A. Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (7)

The synthesis and chemistry of substituted pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes have been treated in a recent article that provides a comprehensive review of the literature through August 1987.[132] Accordingly, the reader is referred to that review for further information and pertinent literature references.

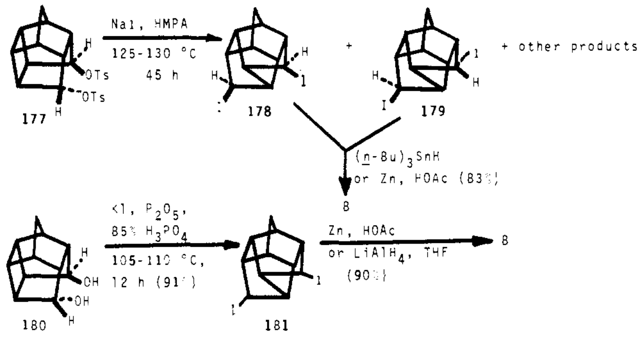
SCHEME 61



SCHEME 62



SCHEME 63

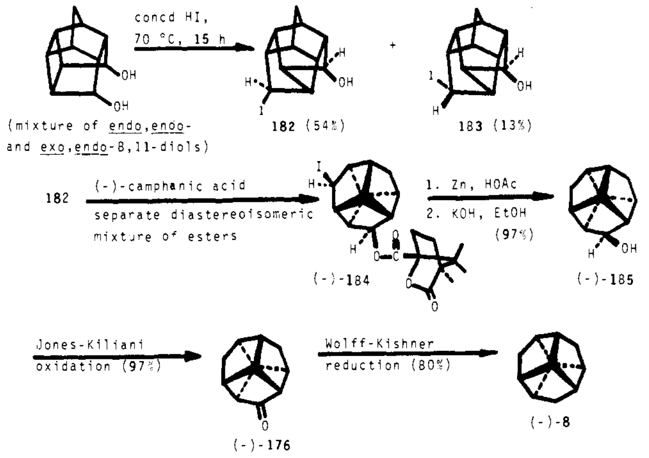


B. Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane [D_3-Trishomocubane (8)]

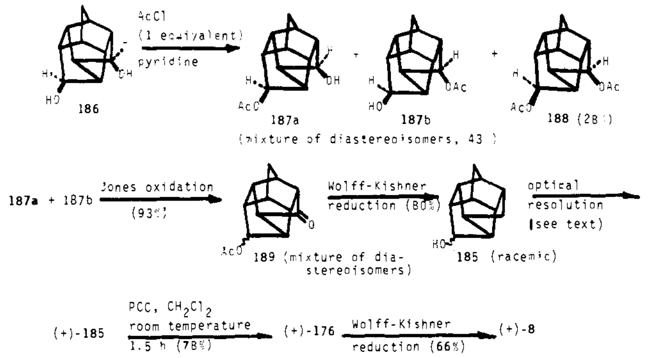
D_3-Trishomocubane (**8**) and its derivatives have been the subject of numerous studies. The parent hydrocarbon is unusual in that it is one of the very few rigid, saturated hydrocarbons that belongs to the chiral point group D_3. Compound **8** also has been shown by molecular mechanics calculations[133,134] to be the $C_{11}H_{14}$ "stabilomer".[135] The first synthesis of **8**, reported in 1970 by Underwood and Ramamoorthy,[136] is shown in Scheme 61. Subsequently, Schleyer and co-workers[134,137] synthesized **8** in 93% yield via $AlBr_3$-catalyzed isomerization of pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**7**). A novel method by which the *endo*-cyclopentadiene–*p*-benzoquinone Diels–Alder adduct[138] could be converted into **8** was reported by Eaton and co-workers (Scheme 62).[139] More recently, two methods were reported wherein **8** was obtained via reductive dehalogenation of iodinated pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecanes (e.g., **178** and **179**, Scheme 63).[140,141] A closely related route for synthesizing **8** was published subsequently by Mehta and Chaudhuri.[142]

Shortly after *rac*-**8** had been synthesized, three research groups independently developed methods for preparing each of the enantiomers of **8** in optically pure form. The absolute configuration of each enantiomer

SCHEME 64



SCHEME 65

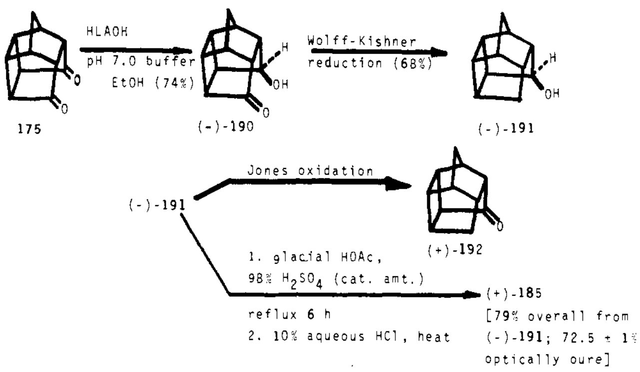


was then determined.[143-146] Helmchen and Staiger[143] separated the mixture of diastereoisomeric esters that resulted from the reaction of *rac*-*endo*-4-hydroxy-*exo*-7-iodopentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane (**182**) with (−)-camphanic acid. Once an individual diastereoisomer, **184**, had been obtained in optically pure form, it was converted into enantiomerically pure (−)-**8** by using the reaction sequence shown in Scheme 64.[143]

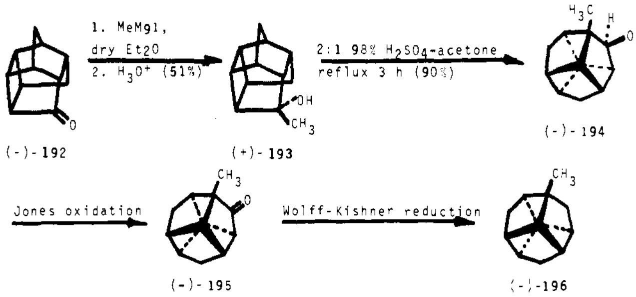
Nakazaki and co-workers[144] utilized Smith and Barborak's procedure[141] to generate *rac*-*cis*-pentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane-4,7-diol (**186**). Attempts at optical resolution of **186** failed; accordingly, the corresponding monoacetate, **187**, was synthesized, and the mixture of diastereoisomeric monoacetates thereby obtained (i.e., **187a** and **187b**) was oxidized to the corresponding mixture of diastereoisomeric keto acetates, **189**. Wolff–Kishner reduction of **189** afforded the corresponding trishomocubanol (*rac*-**185**). Optical resolution of this cage alcohol via the hydrogen phthalate was accomplished by using (+)-2-(1-aminoethyl)naphthalene as the resolving agent; optically pure (+)-**185** was thereby obtained. Oxidation of (+)-**185** by using pyridinium chlorochromate (PCC) in dry methylene chloride afforded (+)-**176**, which, upon Wolff–Kishner reduction, afforded (+)-**8** (Scheme 65).[144]

In addition, Naemura and co-workers[145] have performed an asymmetric reduction of cage diketone **175** by using horse liver alcohol dehydrogenase (HLADH) as catalyst. The optically active keto alcohol, (−)-**190**, thereby obtained was assigned the 1*R*,2*R*,3*R*,5*S*,6*S*,7*S*,9*R*,10*S*,11*R* configuration. Subsequently, (−)-**190** was converted into the corresponding optically active trishomocubanol, (+)-**185**, by using the reaction sequence shown in Scheme 66.[145] Optically active ketone (−)-**192** (Scheme 66) was utilized subsequently to synthesize an optically active 1-alkylpentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane [(−)-**196**, Scheme 67].[145] A similar approach had been reported earlier by Dekker and co-workers[146] for the synthesis of *rac*-**196**.

SCHEME 66



SCHEME 67



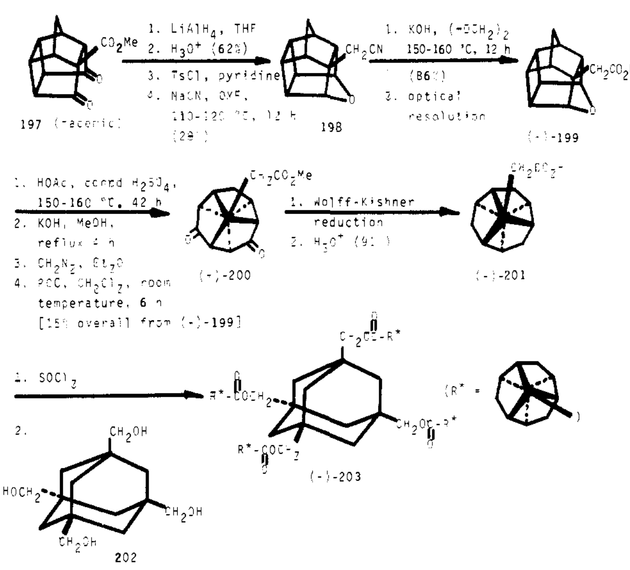
Eaton and Leipzig[147] reported a procedure for optical resolution of trishomocubanone (i.e., *rac*-**176**) via separation of the mixture of diastereoisomers obtained from the reaction of the racemic ketone with *l*-ephedrine. Subsequent acid hydrolysis of each diastereoisomer afforded pure (+)-**176** and (−)-**176**. The absolute configuration of each ketone enantiomer was established by Wolff–Kishner reduction to the corresponding optically active D_3-trishomocubane.

Synthesis of the first enantiomerically pure compounds that possess polyhedral *T* symmetry have been reported by Nakazaki and co-workers.[67a,148-151] These molecules were constructed by placing four optically active 1-pentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecyl groups ($C_3$ subunits) that possess identical chirality as substituents on the 1,3,5,7-positions of adamantane (T_d subunit).[152] This approach is illustrated for the synthesis of (−)-**203** in Scheme 68.[148,149]

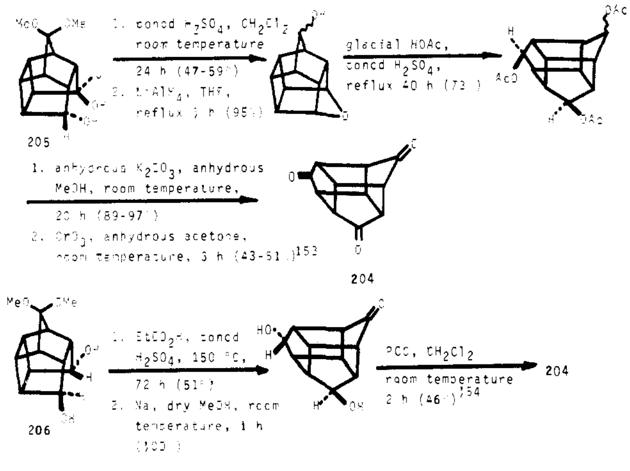
Two routes have been reported for the synthesis of *rac*-D_3-trishomocubanetrione (**204**).[153,154] A 4,4-dimethoxypentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane-8,11-diol (**205** or **206**) was utilized as starting material for both routes. The key step in each synthesis involved acid-promoted Wagner–Meerwein rearrangement from an appropriately substituted pentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane to the corresponding substituted pentacyclo$[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$undecane (Scheme 69).[153,154]

Optical resolution of *rac*-**204** was performed by reaction of this triketone with (*R*,*R*)-2,3-butanediol followed by fractional recrystallization of the mixture of diastereoisomeric trisketals, **207**, thereby obtained from methylene chloride–hexane. Reaction of pure (−)-**207**

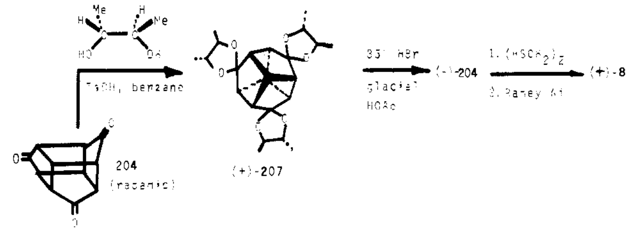
SCHEME 68



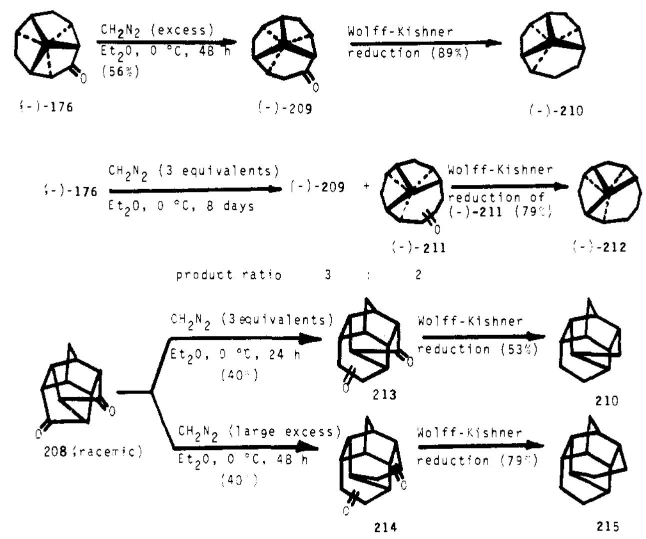
SCHEME 69



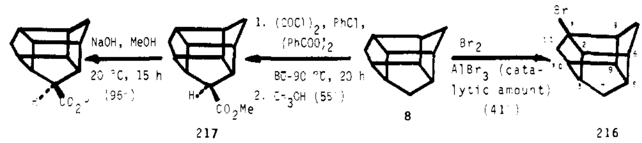
SCHEME 70



SCHEME 71



SCHEME 72



and of pure (+)-207 with 33% HBr in glacial acetic acid afforded optically active (+)-**204** and (−)-**204**, respectively, whose absolute configurations were established by their facile reduction to (−)-**8** and (+)-**8**, respectively (Scheme 70).[153]

rac-D_3-Trishomocubanedione (**208**) has been synthesized by oxidation of diol **186**.[141] Carbocyclic ring expansion of optically active D_3-trishomocubanone (**176**) and of *rac*-**208** have been performed by using diazomethane.[67a,155-157] This approach has been utilized to prepare a series of optically active polycyclic compounds that contain twisted bicyclo[2.2.2]octane moieties. The generic name "triblattanes" has been proposed for these compounds.[67a,158] As examples, optically active [2.1.1]triblattane ["C_2-bismethanotwistane" (**210**)] and [3.1.1]triblattane (**212**) have been synthesized via diazomethane-promoted single- and double-ring expansion of (−)-**176**, respectively. In addition, diazomethane-promoted ring expansion of *rac*-**208** has been utilized as a key step in the synthesis of **210** and of [2.2.1]triblattane (**215**, Scheme 71).[155,156] Additional examples in this regard are presented in a recent review by Nakazaki and Naemura.[158]

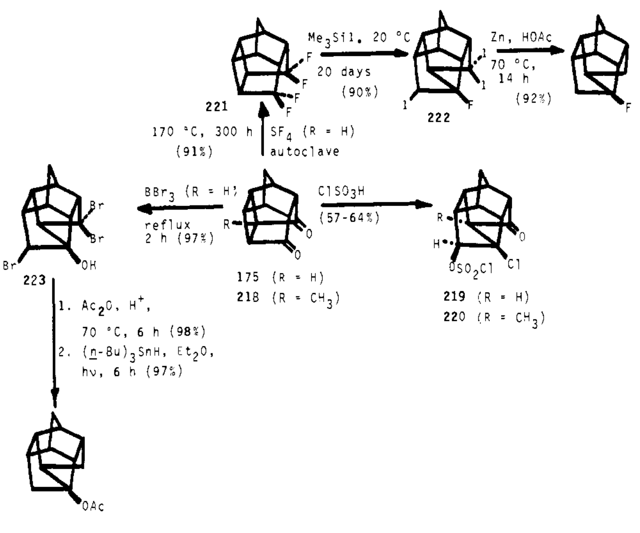
Substituted pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes have been synthesized by direct substitution at peripheral carbon–hydrogen bonds in **8**.[159,160] Bromination of **8** with bromine in the presence of a catalytic amount of aluminum bromide affords the corresponding 1-bromo derivative, **216**.[159] By way of contrast, free radical chlorocarbonylation of **8** results in functionalization at the 4-position (**217**, Scheme 72).[160]

Substituted D_3-trishomocubanes have also been prepared by utilizing pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**175**) and derivatives of this cage diketone as starting materials. Thus, reaction of **175** or its 1-methyl derivative (**218**) with chlorosulfonic acid results in skeletal rearrangement with concomitant formation of trishomocubanones **219** and **220**, respectively.[161] In addition, fluorination of **175** with excess sulfur tetrafluoride results in the formation of the corresponding tetrafluoro derivative (**221**).[162] Subsequent reaction of **221** with trimethylsilyl iodide results in exchange of three of the four fluorine atoms by iodine atom with accompanying rearrangement, thereby affording the corresponding fluorotriiodopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**222**).[162] Finally, a similar rearrangement occurs when **175** is reacted with boron tribromide; the corresponding hydroxytribromopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**223**) is formed in this reaction.[163] These useful reactions are summarized in Scheme 73.

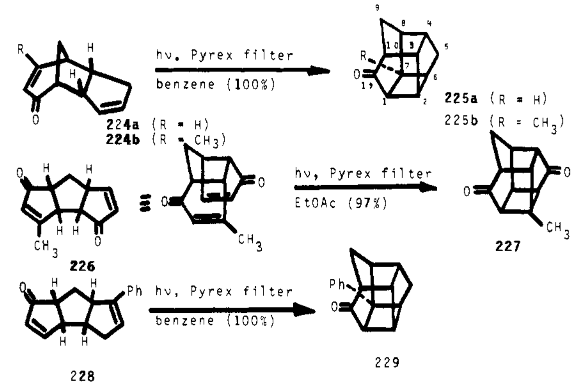
C. Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane (9)

The pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecyl (1,2,4-trishomocubyl) ring system has been synthesized by two routes. The first synthetic route involves [2 + 2] in-

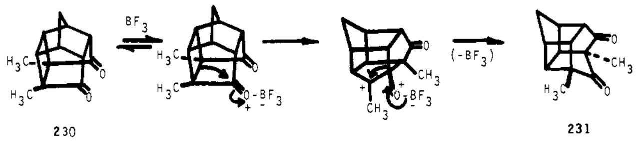
SCHEME 73



SCHEME 74



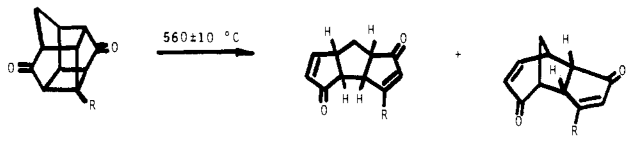
SCHEME 75



tramolecular photocyclization of a suitably constructed polycyclic diene precursor (e.g., **224** → **225**,[164] **226** → **227**,[165,166] and **228** → **229**,[167] Scheme 74). The second synthetic route involves the Lewis acid promoted rearrangement of a substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (i.e., **230** → **231**, Scheme 75).[168,169]

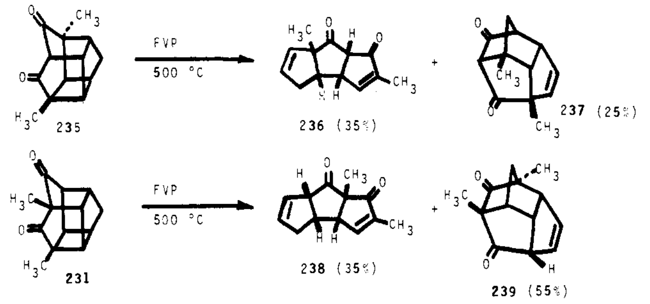
Thermal cycloreversions of substituted 1,2,4-trishomocubanes to afford *cis,syn,cis*-tricyclo[6.3.0.0^{2,6}]undecanes and/or substituted tricyclo[5.3.1.0^{2,6}]undecadienes have been reported. Thus, flash vacuum pyrolyses of 2-substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane-5,11-diones **227** and **232–234** proceed in the manner shown in Scheme 76.[169] The data shown in Scheme 76 indicate that the regiochemistry of thermal fragmentation of the cyclobutane ring in the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane ring system is influenced markedly by substituents at C(2). [Compare the product distribution obtained via flash vacuum pyrolysis of **227** and **232** (R = alkyl) with the corresponding product distribution obtained via flash vacuum pyrolysis of **233** and **234** (R = aryl)]. In an effort to rationalize this observation, it was suggested[169] that the C(2)–C(6) bond might be weaker in **233** and **234** (relative to the corresponding bond in **227** and **232**) due to bond lengthening that results from through-bond interaction[170] of this σ-bond with the aryl group in **233** and in **234**.

SCHEME 76

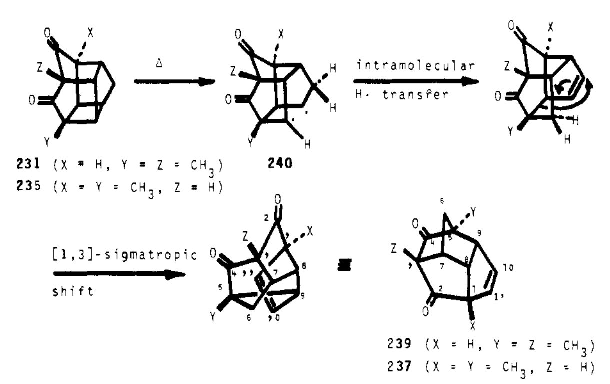


	(% yield)	(% yield)
227 (R = CH_3)	8	70
232 (R - $CH_2CH=CH_2$)	-	60
233 (R = Ph)	80	-
234 (R = p-$MeOC_6H_4$)	76	-

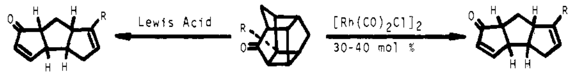
SCHEME 77



SCHEME 78



SCHEME 79



Product (% yield)	Conditions	Reactant	Conditions	Product (% yield)
241 (ca. 100)	BF_3, benzene reflux 6 h	**225a** (R = H)	diglyme, 160 °C	**241** (0)
242 (ca. 100)	TsOH, benzene room temperature 6 h	**225b** (R = CH_3)	diglyme, 160 °C	**242** ("good yield")
228 (ca. 100)	BF_3, benzene room temperature 30 minutes	**229** (R = Ph)	benzene, 80 °C	**228** ("good yield")

In addition, flash vacuum pyrolysis of 1,8-dimethyl- and of 1,10-dimethylpentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane-9,11-diones (**235** and **231**, respectively) affords the corresponding *cis,syn,cis*-tricyclo[6.3.0.0^{2,6}]undecanes (**236** and **238**, respectively) along with novel, tetracyclic rearranged products (i.e., substituted tetracyclo[6.3.0.0^{3,7}.0^{5,9}]undec-10-ene-2,4-diones **237** and **239**, respectively, Scheme 77).[169] A stepwise mechanism that involves the formation of an intermediate diradical, **240**, was suggested to account for the formation of tetracyclic products **237** and **239** in these reactions (Scheme 78).[169]

Ogino and co-workers have studied valence isomerizations of 7-substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecan-11-ones **225a**, **225b**, and **229** to the corresponding *cis,syn,cis*-tricyclo[6.3.0.0^{2,6}]undecanes (**241**, 242, and 228, respectively). These valence isomerizations occur when each pentacyclic substrate is treated with Lewis acids or proton acids[165] or, with the lone exception of **225a**, when the substrate is reacted with rhodium dicarbonyl chloride dimer[171] under the conditions shown in Scheme 79. In the case of the Rh(I)-promoted valence isomerizations of **225a**, **225b**, and **229**, the relative reactivity order R = Ph > CH_3 ≫ H was observed. The pronounced rate acceleration caused by the 7-phenyl group in **229** relative to the corresponding 7-methyl-substituted compound (i.e., **225b**) might suggest that positive charge (which is better delocalized by phenyl than by methyl substitution) develops at C(7) in the transition state for this process. However, a corresponding study of the Rh(I)-promoted valence isomerization of **225b** (R = CD_3) revealed the operation of only a small secondary β-deuterium isotope effect (k_H/k_D = 1.04). This result argues against a cationic transition state for this process in which a significant degree of rehybridization (from sp^3 to sp^2) occurs at C(7). By way of contrast, valence isomerization of **225b** (R = CH_3 vs R = CD_3), when catalyzed by *p*-toluenesulfonic acid in deuteriochloroform at 30 °C, proceeds with a significantly larger secondary β-deuterium isotope effect (k_H/k_D = 1.15). Clearly, development of cationic character at C(7) is much greater in the transition state for the acid-catalyzed valence isomerization of **225b** when compared with the corresponding Rh(I)-promoted valence isomerization process.[171]

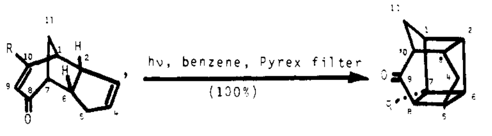
As an alternative to the cationic mechanism, Ogino and co-workers[171] suggested that these transition-metal-promoted valence isomerizations may instead proceed in concerted fashion. For example, the C(7) phenyl group in **229**, by operating through a HOMO(π_{CC}) that possesses the correct orbital symmetry, can donate electron density to a LUMO(σ^*_{CC}) of the cyclobutane ring in the transition state, thereby lowering the activation energy in the reaction of **229** with Rh(I). It should be noted that the rates of the acid-catalyzed reactions are roughly 3 orders of magnitude greater than the corresponding Rh(I)-promoted valence isomerization of **225a**, **225b**, and **229**.[165,171]

The valence isomerizations presented in Schemes 76, 77, and 79 provide useful routes for preparing substituted cis,syn,cis linear triquinanes. Mehta and co-workers[94,95,172] also have utilized substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones as precursors to cis,syn,cis linear triquinanes. The resulting triquinanes were used subsequently to synthesize polyquinane natural products (e.g., coriolin, hirsutene, and capnellene).[173] The cis,syn,cis linear triquinanes that result from valence isomerization of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecanes possess markedly different substitution patterns when compared with the corresponding species produced from substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione precursors. The two approaches, therefore, are complementary.

D. Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecane (10)

Substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecanes **247–250** have been synthesized by [2 + 2] photocyclizations of 10-substituted tetracyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-ones **243–246** (Scheme 80).[164,174]

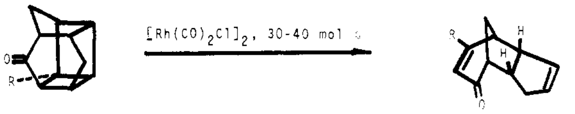
SCHEME 80



243 (R = H)
244 (R = CH_3)
245 (R = OCH_3)
246 (R = Ph)

247 (R = H)
248 (R = CH_3)
249 (R = OCH_3)
250 (R = Ph)

SCHEME 81



Reactant	Conditions	Product
247 (R = H)	diglyme, 120 °C	**243** (R = H)
248 (R = CH_3)	diglyme, 160 °C	244 (R = CH_3)
250 (R = Ph)	diphenyl ether, 190 °C	246 (R = Ph)

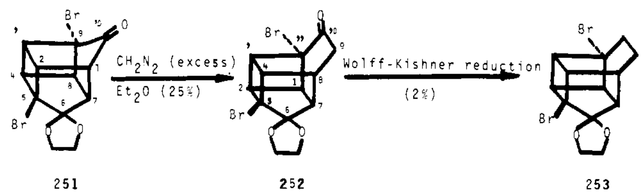
Rh(I)-promoted valence isomerizations of **247**, **248**, and **250** have been studied by Ogino and co-workers (Scheme 81).[171] Particularly noteworthy is the observed effect of 7-substituents upon the rate of this reaction. In contrast to the results obtained for Rh(I)-promoted valence isomerizations of **225a**, **225b**, and **229** (Scheme 79), the presence of a 7-methyl or 7-phenyl group in pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecan-9-one (**247**) was found to severely *retard* the corresponding valence isomerization process (i.e., k_{rel} at 40 °C was found to be **247**:**248**:**250** = 1:0.011:0.0024). Also, it was noted[171] that **229** reacts considerably faster with Rh(I) than does **250**, despite the fact that the parent hydrocarbon of **250** (i.e., **10**) is calculated to be more strained than the parent hydrocarbon of **229** (i.e., **9**) by ca. 10 kcal/mol.[134]

In order to explain these observations, Ogino and co-workers[171] suggested that rate-determining attack of the Rh(I) complex on **247** and on 7-substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecan-9-ones **248** and **250** occurs preferentially at the C(6)–C(7) bond in the substrate. Here, the primary function of the 7-methyl group in **248** and of the 7-phenyl group in **250** is to exert a steric effect that impedes attack by the approaching reagent, thereby retarding the rate of Rh(I)-promoted valence isomerization in these substrates (vis-à-vis the corresponding valence isomerization of **247**). This differs fundamentally from the mode of operation of substituent effects in Rh(I)-promoted valence isomerizations of 7-substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecan-11-ones (e.g., **225a**, **225b**, and **227**; cf. section IV.C).[171]

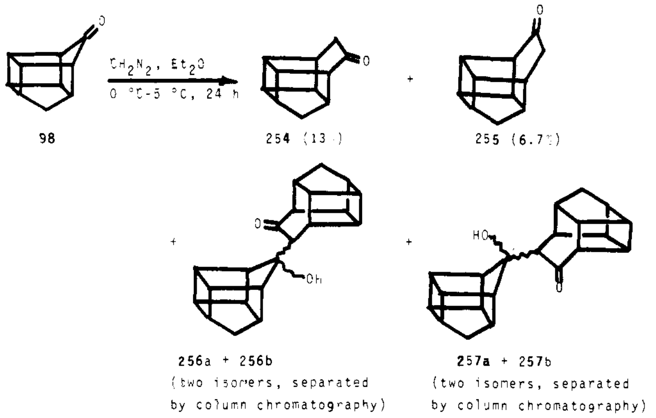
E. Pentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,8}]undecane [C_1-Homobasketane, [2.1.0]Triblattane (11)]

A useful synthetic entry into the C_1-homobasketane ring system has been achieved by diazoalkane-promoted ring expansion[42] of substituted 1,3-bishomocubanones. An example is provided by the ring expansion of **251**; reaction of this compound with excess diazomethane afforded **252** in 25% yield (Scheme 82).[39] As was found to be the case for the corresponding one-carbon homologation of substituted 1-bromohomocubanones (section II.C), regiospecific C(1)–C(10) bond migration in **251** which occurs as a result of its reaction with diazomethane is controlled by the presence of the 9-bromo substituent. Once again, the presence of the

SCHEME 82



SCHEME 83



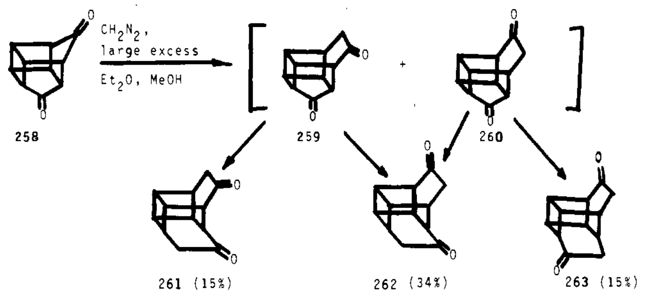
9-halogen atom effectively suppresses migration of the terminus to which it is attached.[40-42] Subsequent Wolff–Kishner reduction of **252** afforded **253** in disappointingly low yield (2%).

Other examples wherein diazomethane-promoted ring expansion of bishomocubane derivatives has been utilized to synthesize substituted C_1-homobasketanes have been reported by Hirao and co-workers.[107-109] Thus, reaction of 1,3-bishomocubanone (**98**) with ethereal diazomethane afforded a complex mixture of products. Chromatographic purification of the crude product mixture on silica gel afforded two fractions (47% and 43% yield, respectively). Further chromatographic purification of the first fraction afforded two isomeric C_1-homobasketanones (**254** and **255**) in 13% and 6.7% yield, respectively. Similar chromatographic purification of the second fraction afforded four pure isomeric dimers, **256a**, **256b**, **257a**, and **257b**. These products appear to have resulted from subsequent aldol condensation of each of the initially formed C_1-homobasketanones with excess 1,3-bishomocubanone. These results are summarized in Scheme 83.[109]

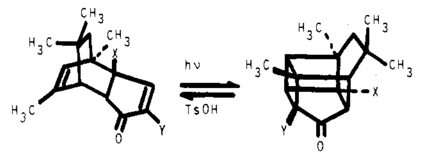
Addition of potential proton donors (e.g., CH_3OH) to the reaction medium was found to increase the yield of monohomologation product at the expense of dimer formation in these reactions. This result was interpreted in terms of solvent trapping of a betaine intermediate (formed via addition of diazomethane to the ketone carbonyl group in the substrate). This trapping process competes effectively with prototropic shift that would result in formation of an ylide-type structure that is capable of undergoing aldol condensation with unreacted starting material.[109]

Hirao and co-workers[109] also have investigated the reaction of 1,3-bishomocubanedione (**258**) with ethereal diazomethane (large excess) in the presence of methanol. Three products (**261**–**263**) were formed in this reaction in yields of 15%, 34%, and 15%, respectively. Presumably, the two possible C_1-homobasketanediones, **259** and **260**, were formed as intermediates in this reaction but did not survive in the presence of excess diazomethane (Scheme 84).[109]

SCHEME 84



SCHEME 85



264a (X = CO_2Et, Y = H)
264b (X = Y = H)
264c (X = CO_2Me, Y = CH_3)
264d (X = H, Y = CH_3)

265a (X = CO_2Et, Y = H)
265b (X = Y = H)
265c (X = CO_2Me, Y = CH_3)
265d (X = H, Y = CH_3)

Photochemical [2 + 2] cyclizations that afford C_1-homobasketane derivatives have been studied as potential solar energy storage systems.[175] Thus, photocyclization of each of the dienes **264a**–**d** afforded the corresponding cage system (**265a**–**d**, respectively) in quantitative yield. The corresponding acid-promoted cycloreversion reactions also proceeded quantitatively (Scheme 85).[175]

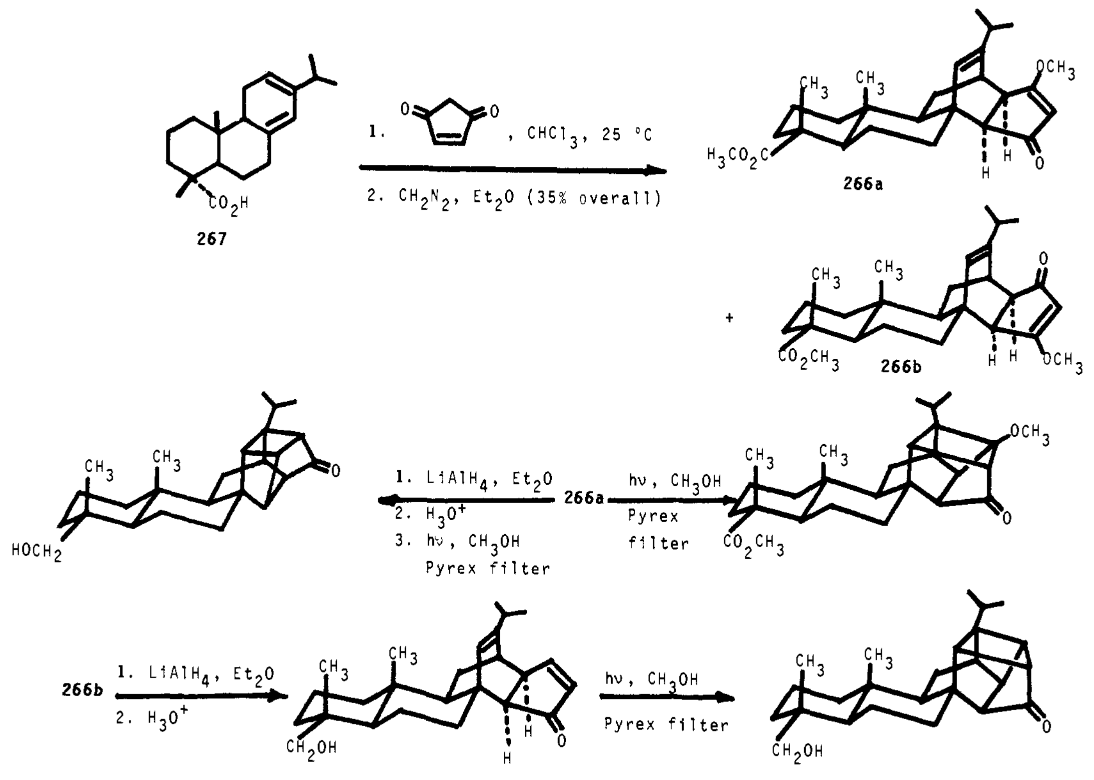
Similarly, intramolecular [2 + 2] photocyclizations have been studied in complex molecules (e.g., **266a** and **266b**) that are derived from levopimaric acid (**267**).[176-178] Some transformations of **266a** and of **266b** that result in the formation of complex, substituted C_1-homobasketanes are shown in Scheme 86.[177]

As part of their synthesis of optically active triblattanes,[67a,158] Nakazaki and co-workers[157] have prepared (−)-**11** (i.e., optically active [2.1.0]triblattane). A key step in their synthesis of (−)-**11** involved diazomethane-promoted ring expansion of optically active 1,3-bishomocubanone mono(ethylene ketal), (+)-**97**[65-67] (Scheme 87).[157] More recently, (−)-[2.1.0]triblattan-4-one (i.e., (−)-**269**) has been used as starting material for the synthesis of other optically active [*m*.1.0]triblattanes (where *m* = 3–5) and [*m*.2.0]triblattanes (where *m* = 3–6).[179]

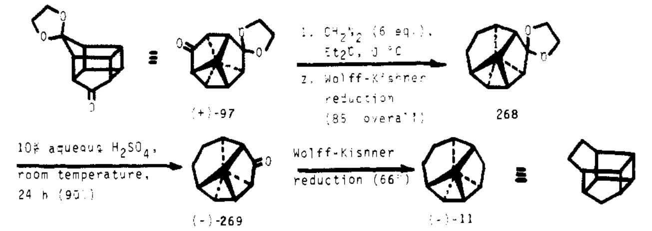
The reaction of *rac*-**11** with $[Rh(CO)_2Cl]_2$ has been studied.[83] Two products, **270** and **271**, were obtained when a benzene solution of **11** was heated with the Rh(I) complex in a pressure tube at 80 °C for 72 h. It is likely that this reaction proceeds via oxidative insertion of Rh(I) into the C(2)–C(3) σ-bond of **11** with concomitant formation of an intermediate dinuclear acylrhodium complex. This complex is analogous to the intermediate, **113**, which results from the corresponding reaction of 1,3-bishomocubane with $[Rh(CO)_2Cl]_2$ (see Scheme 36).[83] The course of the reaction of **11** with $[Rh(CO)_2Cl]_2$ is summarized in Scheme 88.

Finally, photochemical and thermal decarbonylations of substituted [2.1.0]triblattan-4-ones have been studied.[180] Thus, the endo Diels–Alder adduct, **272**, of 1,3-cyclohexadiene (diene) to 2,5-dimethyl-3,4-di-

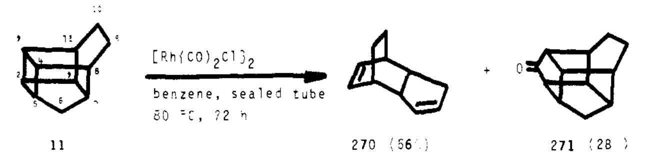
SCHEME 86



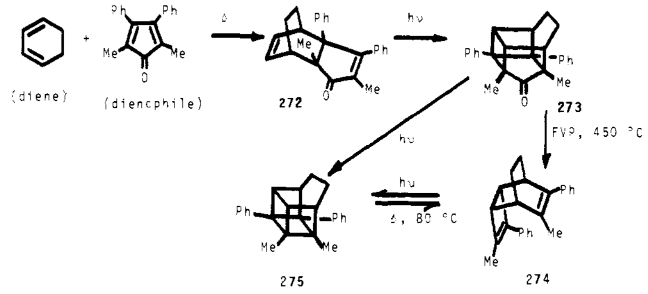
SCHEME 87



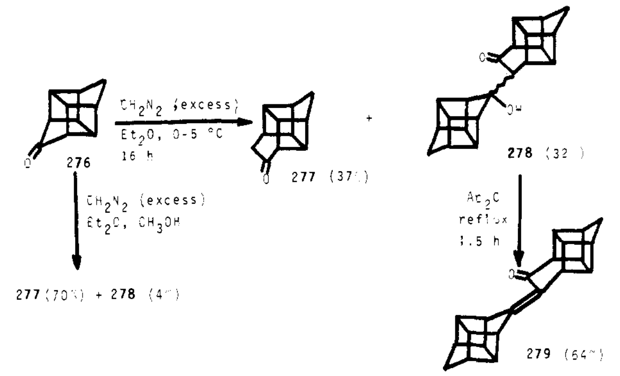
SCHEME 88



SCHEME 89



SCHEME 90

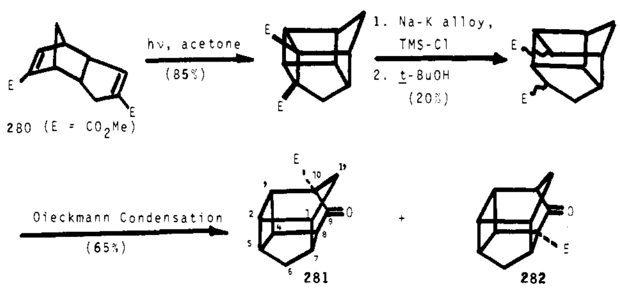


phenylcyclopentadienone (dienophile) undergoes facile [2 + 2] intramolecular photocyclization to afford 1,2-diphenyl-5,7-dimethylpentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,8}]undecan-6-one (**273**). Flash vacuum pyrolysis of **273** through a quartz tube at 450 °C afforded diene **274**. Alternatively, photodecarbonylation of **273** afforded cage hydrocarbon **275** in 16% yield. Subsequent thermolysis of **275** occurred at 80 °C to afford diene **274**. Irradiation of **274** afforded cage hydrocarbon **275** in quantitative yield. These reactions are summarized in Scheme 89.[180] As noted previously (section III.A), the reversible (photothermal) transformation **274** $\rightleftarrows$ **275** has been studied as a model for solar energy storage.[55]

F. Pentacyclo[5.4.0.0^{2,6}.0^{3,9}.0^{4,8}]undecane (12)

Hirao and co-workers[108,109] have synthesized derivatives of **12** by diazomethane-promoted ring expansion of 1,4-bishomocubanone (**276**). Thus, reaction of **276**[91] with excess ethereal diazomethane at 0–5 °C for 16 h afforded pentacyclo[5.4.0.0^{2,6}.0^{3,9}.0^{4,8}]undecan-10-one (**277**, 37%) along with a dimeric β-hydroxy ketone, **278** (32%).[109] Compound **278** most likely resulted from crossed aldol condensation between **276** and **277**. Subsequent dehydration of **278** afforded the corresponding enone, **279** (64% yield, Scheme 90). Once again, as was found to be the case for the reaction of **98** with diazomethane (Scheme 83), the presence of a proton donor (e.g., methanol) was found to suppress the formation of the aldol condensation product in the corresponding reaction of **276** with diazomethane (Scheme 90).[109]

SCHEME 91



G. Pentacyclo[$5.4.0.0^{2,5}.0^{3,10}.0^{4,8}$]undecane (13)

To our knowledge, synthesis of this ring system has not been reported in the literature. An approach to the synthesis of substituted pentacyclo[$5.4.0.0^{2,5}.0^{3,10}.0^{4,8}$]undecanes 281 and 282 that starts with the readily available endo dimer of carbomethoxycyclopentadiene [i.e., "Thiele's ester" (280)][63,64] is shown in Scheme 91.[181]

H. Compounds 14–20 (Table 1)

To the best of our knowledge, no synthesis of any of these trishomocubanes or derivatives of these trishomocubyl ring systems has been reported in the literature.

V. *Epilogue*

And so, our story ends
Or, rather, pauses for a time
Like life itself,
With no beginning and no end.
We only stop to catch our breath
And smell a rose or two
And then continue on our way.
We lurch along a path
That cannot always be discerned
And wonder what will lie ahead.

VI. *Acknowledgments*

I gratefully acknowledge receipt of financial support of our research on the synthesis and chemistry of bishomocubanes and trishomocubanes from the following agencies: the Robert A. Welch Foundation (Grant B-963), the Air Force Office of Scientific Research (Grants AFOSR-84-0085 and AFOSR-88-0132), the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NY, and the University of North Texas Faculty Research Committee. Helpful discussions with Dr. Wendell L. Dilling are gratefully acknowledged. Finally, I thank Drs. Paritosh R. Dave, Singam Pulla Reddy, and Vuligonda Vidyasagar for having proofread and constructively criticized the manuscript of this review.

VII. *References*

(1) Stirling, C. J. M. *Tetrahedron* **1985**, *41*, 1613.
(2) (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1984**, *86*, 962, 3157. (b) Cubane is reviewed elsewhere in this issue: Griffin, G. W.; Marchand, A. P. *Chem. Rev.* **1989**, *89*, 997.
(3) Paquette, L. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 2584.
(4) Cargill, R. L.; King, T. Y.; Sears, A. B.; Willcott, M. R. *J. Org. Chem.* **1971**, *36*, 1423.
(5) Barborak, J. C.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 3080.
(6) (a) Dauben, W. G.; Reitman, L. N. *J. Org. Chem.* **1975**, *40*, 841. (b) Warrener, R. N.; Anderson, C. M.; McCay, I. W.; Paddon-Row, M. N. *Aust, J. Chem.* **1977**, *30*, 1481.
(7) Dauben, W. G.; Whalen, D. L. *Tetrahedron Lett.* **1966**, 3743.
(8) Chapman, N. B.; Key, J. M.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 3860.
(9) (a) Dunn, G. L.; DiPasquo, V. J.; Hoover, J. R. E. *Tetrahedron Lett.* **1966**, 3737. (b) Dunn, G. L.; DiPasquo, V. J.; Hoover, J. R. E. *J. Org. Chem.* **1968**, *33*, 1454.
(10) Paquette, L. A.; Ward, J. S. *J. Org. Chem.* **1972**, *37*, 3569.
(11) Klunder, A. J. H.; Ariaans, G. J. A.; van der Loop, E. A. R. M.; Zwanenburg, B. *Tetrahedron* **1986**, *42*, 1903.
(12) Schleyer, P. von R.; Harper, J. J.; Dunn, G. L.; DiPasquo, V. J.; Hoover, J. R. E. *J. Am. Chem. Soc.* **1967**, *89*, 698.
(13) Scherer, K. V., Jr.; Lunt, R. S., III; Ungefug, G. A. *Tetrahedron Lett.* **1965**, 1199.
(14) Chin, C. G.; Cuts, H. W.; Masamune, S. *Chem. Commun.* **1966**, 880.
(15) For a review, see: Chenier, P. J. *J. Chem. Educ.* **1978**, *55*, 286.
(16) (a) Loftfield, R. B. *J. Am. Chem. Soc.* **1950**, *72*, 632. (b) Loftfield, R. B. *J. Am. Chem. Soc.* **1951**, *73*, 4707.
(17) For a review, see: Selman, S.; Eastham, J. F. *Q. Rev., Chem. Soc.* **1960**, *14*, 221.
(18) Hamlin, K. E.; Weston, A. W. *Org. React.* **1957**, *9*, 1.
(19) Griffin, G. W.; Chaudhuri, A. L.; Reichel, L. W.; Breyer, R. A.; Condon, M. M.; Elhajj, T.; Lankin, D. C.; Stevens, E. D.; Li, Y. J. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 30–Sep 4, 1987; American Chemical Society: Washington, DC, 1987; ORGN-11.
(20) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.
(21) Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285.
(22) Ōsawa, E.; Aigami, K.; Inamoto, Y. *J. Org. Chem.* **1977**, *43*, 2621.
(23) (a) Politzer, P.; Domelsmith, L. N.; Abrahmsen, L. *J. Phys. Chem.* **1984**, *88*, 1752. (b) This statement applies to the C(2)–C(5), C(3)–C(4), C(4)—C(7), and C(5)–C(6) bonds in 1, all of which are equivalent.
(24) (a) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 281. (b) Ōsawa, E.; Schleyer, P. von R.; Chang, L. W. K.; Kane, V. V. *Tetrahedron Lett.* **1974**, 4174. (c) Paquette, L. A.; Ward, J. S.; Boggs, R. A.; Farnham, W. B. *J. Am. Chem. Soc.* **1975**, *97*, 1101. (d) Paquette, L. A.; Boggs, R. A.; Ward, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 1118.
(25) (a) For reviews, see: (a) Halpern, J. in *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 705–730. (b) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461. (c) Mango, F. D. *Coord. Chem. Rev.* **1976**, *10*, 109.
(26) (a) Ōsawa, E.; Schneider, I.; Toyne, K. J.; Musso, H. *Chem. Ber.* **1986**, *119*, 2350. (b) Stober, R.; Musso, H.; Ōsawa, E. *Tetrahedron* **1986**, *41*, 1757. (c) Toyne, K. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1346.
(27) Gassman, P. G.; Lumb, J. T.; Zalar, F. V. *J. Am. Chem. Soc.* **1967**, *89*, 946.
(28) For a review, see: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205.
(29) (a) Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron Lett.* **1971**, 1721. (b) Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1973**, *29*, 1683. (c) Empirical force field calculations have been utilized to rationalize the observed regiochemistry of homoketonizations and other apparently thermodynamically controlled cage ring-opening processes. See: Ōsawa, E.; Aigami, K.; Inamoto, Y. *J. Chem. Soc., Perkin Trans. 2* **1979**, 181.
(30) (a) Miller, R. D.; Dolce, D. *Tetrahedron Lett.* **1973**, 1151. (b) Miller, R. D.; Dolce, D. *Tetrahedron Lett.* **1977**, 1023.
(31) (a) Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron Lett.* **1972**, 2383. (b) Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1975**, *31*, 1419.
(32) Mergelsberg, I.; Langhals, H.; Rüchardt, C. *Chem. Ber.* **1983**, *116*, 360.
(33) Dauben, W. G.; Whalen, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 4739.
(34) Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1973**, *29*, 161.
(35) Mak, T. C. W.; Yip, Y. C.; Luh, T.-Y. *Tetrahedron* **1986**, *42*, 1981.
(36) Mehta, G.; Rao, K. S.; Suri, S. C.; Cameron, T. S.; Chan, C. *J. Chem. Soc., Chem. Commun.* **1980**, 650.
(37) (a) Masamune, S.; Cuts, H.; Hogben, M. G. *Tetrahedron Lett.* **1966**, 1017. (b) A three-step synthesis of basketane from cyclooctatetraene that proceeds via the cyclooctatetraene–acrylonitrile cycloadduct has been reported. See: Mehta, G.; Srikrishna, A.; Suri, S. C. *J. Org. Chem.* **1980**, *45*, 5375.
(38) Gassman, P. G.; Yamaguchi, R. *J. Org. Chem.* **1978**, *43*, 4654.
(39) van Seters, A. J. C.; Buza, M.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1981**, *37*, 1027.
(40) Dave, V.; Warnhoff, E. W. *J. Org. Chem.* **1983**, *48*, 2590.
(41) See: Marchand, A. P.; Annapurna, P.; Reddy, S. P.; Watson, W. H.; Nagl, A. *J. Org. Chem.* **1989**, *54*, 187.

(42) For a review of one-carbon ring expansions of bridged bicyclic ketones, see: Krow, G. R. *Tetrahedron* **1987**, *43*, 3.
(43) Paquette, L. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 2584.
(44) (a) Paquette, L. A.; Beckley, R. S.; Truesdell, D.; Clardy, J. *Tetrahedron Lett.* **1972**, 4913. (b) Paquette, L. A.; Beckley, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 1084.
(45) (a) Dauben, W. G.; Buzzolini, M. G.; Schallhorn, C. H.; Whalen, D. L. *Tetrahedron Lett.* **1970**, 787. (b) Dauben, W. G.; Kielbania, A. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 7345.
(46) (a) Paquette, L. A.; Beckley, R. S.; Farnham, W. B. *J. Am. Chem. Soc.* **1975**, *97*, 1089. (b) Yokoyama, K.; Saegusa, Y.; Miyashi, T.; Kabuto, C.; Mukai, T. *Chem. Lett.* **1984**, 89.
(47) Paquette, L. A.; Boggs, R. A.; Farnham, W. B.; Beckley, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 1112.
(48) Takaya, H.; Yamakawa, M.; Noyori, R. *Chem. Lett.* **1973**, 781.
(49) Sasaki, N. A.; Zunker, R.; Musso, H. *Chem. Ber.* **1973**, *106*, 2992.
(50) (a) Musso, H. *Chem. Ber.* **1975**, *108*, 337. (b) However, Musso[50a] has reported that hydrogenation–hydrogenolysis of methanolic basketene (**75**) affords **76** (1%), **78** (60%), and a third product, "isotwistane" (24%).
(51) Ōsawa, E.; Schleyer, P. von R.; Chang, L. W. K.; Kane, V. V. *Tetrahedron Lett.* **1974**, 4189.
(52) Engler, E. M.; Andose, J. D.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(53) Klunder, A. J. H.; van Seters, A. J. C.; Buza, M.; Zwanenburg, B. *Tetrahedron* **1981**, *37*, 1601.
(54) Mehta, G.; Srikrishna, A. *Indian J. Chem., Sect. B* **1980**, *19B*, 997.
(55) Mukai, T.; Yamashita, Y. *Tetrahedron Lett.* **1978**, 357.
(56) Okada, K.; Hisamitsu, K.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1980**, 941.
(57) Mukai, T.; Sato, K.; Yamashita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 670.
(58) (a) Okada, K.; Hisamitsu, K.; Mukai, T. *Tetrahedron Lett.* **1981**, 1251. (b) Okada, K.; Hisamitsu, K.; Miyashi, T.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1982**, 974.
(59) Hasegawa, E.; Mukai, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3391.
(60) Related studies: (a) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1971**, *103*, 4977. (b) Roth, H. D.; Schilling, M. L. M.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* **1983**, *24*, 5815. (c) Takahashi, Y.; Sato, K.; Miyashi, T.; Mukai, T. *Chem. Lett.* **1984**, 1553. (d) Hasegawa, F.; Okeda, K.; Mukai, T. *J. Am. Chem. Soc.* **1984**, *106*, 6852. (e) Yamashita, Y.; Ikeda, H.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 6682 and references cited therein.
(61) (a) Cookson, R. C.; Hudec, J.; Williams, R. O. *Tetrahedron Lett.* **1960**, *No. 22*, 29. (b) For a review of intramolecular [2 + 2] photocyclization reactions, see: Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373.
(62) Synthesis of **4** via intramolecular [2 + 2] photocyclization of *endo*-dicyclopentadiene: (a) Schenck, G. O.; Steinmetz, R. *Chem. Ber.* **1963**, *96*, 520. (b) Dilling, W. L.; Reineke, C. E. *Org. Photochem. Synth.* **1971**, *1*, 85.
(63) Thiele, J. *Chem. Ber.* **1901**, *34*, 68.
(64) Dunn, G. L.; Donohue, J. K. *Tetrahedron Lett.* **1968**, 3485.
(65) Nakazaki, M.; Naemura, K. *J. Org. Chem.* **1977**, *42*, 2985.
(66) Nakazaki, M.; Naemura, K.; Nakahara, S. *J. Org. Chem.* **1978**, *43*, 4745.
(67) (a) For a review of the synthesis and sterochemistry of chiral organic molecules with high symmetry, see: Nakazaki, M. *Top. Stereochem.* **1974**, *15*, 199. (b) See also: Klunder, A. J. H.; Huizinga, W. B.; Hulshof, A. J. M.; Zwanenburg, B. *Tetrahedron Lett.* **1986**, *27*, 2543.
(68) Fuchs, B. *J. Am. Chem. Soc.* **1971**, *93*, 2544.
(69) Pazhenchevsky, B.; Fuchs, B. *Tetrahedron Lett.* **1972**, 3047.
(70) Fuchs, B.; Pazhenchevsky, B.; Pasternak, M. *Tetrahedron Lett.* **1972**, 3051.
(71) Klinsmann, U.; Gauthier, J.; Schaffner, K.; Pasternak, M.; Fuchs, B. *Helv. Chim. Acta* **1972**, *55*, 2643.
(72) Houk, K. N.; Northington, D. J. *Tetrahedron Lett.* **1972**, 303.
(73) Fuchs, B. *Isr. J. Chem.* **1980**, *20*, 203.
(74) (a) Fuchs, B.; Pasternak, M.; Pazhenchevsky, B. *J. Org. Chem.* **1981**, *46*, 2017. (b) Fuchs, B.; Pasternak, M.; Pazhenchevsky, B. *Tetrahedron* **1980**, *36*, 3443 and references cited therein.
(75) Fuchs, B.; Drucker, C.; Lidor, R. *J. Org. Chem.* **1981**, *46*, 1479.
(76) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
(77) Marchand, A. P.; Annapurna, G. S.; Vidyasagar, V.; Flippen-Anderson, J. L.; Gilardi, R.; George, C.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 4781.
(78) Paquette and co-workers have synthesized 1,3-bishomocubanedione by a lengthy procedure, one step of which involves transoximation of *endo*-dicyclopentadienone dioxime. See: Paquette, L. A.; Davis, R. F.; James, D. R. *Tetrahedron Lett.* **1974**, 1615.
(79) Vogel, E.; Wyes, E. G. *Chem. Ber.* **1965**, *98*, 3680.
(80) Marchand, A. P.; Reddy, D. S. *J. Org. Chem.* **1984**, *49*, 4078.
(81) Luh, T.-Y. *Tetrahedron Lett.* **1977**, 2951.
(82) Klunder, A. J. H.; Ariaans, G. J. A.; Zwanenburg, B. *Tetrahedron Lett.* **1984**, *25*, 5457.
(83) Zlotogorski, C.; Blum, J.; Ōsawa, E.; Schwarz, H.; Höhne, G. *J. Org. Chem.* **1984**, *49*, 971.
(84) Hirao, K.-i.; Iwakuma, T.; Taniguchi, M.; Abe, E.; Yonemitsu, O.; Date, T.; Kotera, K. *J. Chem. Soc., Chem. Commun.* **1974**, 691.
(85) Hirao, K.-i.; Iwakuma, T.; Taniguchi, M.; Yonemitsu, O.; Date, T.; Kotera, K. *J. Chem. Soc., Perkin Trans. 1* **1980**, 163.
(86) Calculations were based upon the Allinger 1971–1972 force fields. See: (a) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637. (b) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734. (c) Allinger, N. L.; Tribble, M. T.; Miller, M. A. *Tetrahedron* **1972**, *28*, 1173.
(87) Bosse, D.; de Meijere, A. *Tetrahedron Lett.* **1977**, 1155.
(88) Bosse, D.; de Meijere, A. *Chem. Ber.* **1978**, *111*, 2223.
(89) (a) Mehta, G.; Pandey, P. N.; Usha, R.; Venkatesan, K. *Tetrahedron Lett.* **1976**, 4209. (b) Mehta, G.; Pandey, P. N.; Usha, R.; Venkatesan, K. *Indian J. Chem., Sect. B* **1981**, *20B*, 177.
(90) Dilling, W. L.; Reineke, C. E. *Tetrahedron Lett.* **1967**, 2547.
(91) Dilling, W. L.; Reineke, C.; Plepys, R. A. *J. Org. Chem.* **1969**, *34*, 2605.
(92) Klunder, A. J. H.; de Valk, W. C. G. M.; Verlaak, J. M. J.; Schellekens, J. W. M.; Noordik, J. H.; Parthasarathi, V.; Zwanenburg, B. *Tetrahedron* **1985**, *41*, 963.
(93) Ivanov, P. M.; Ōsawa, E.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1985**, *41*, 975.
(94) Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543.
(95) Mehta, G. *J. Chem. Educ.* **1982**, *59*, 313.
(96) Brown, R. F. C.; Browne, N. R.; Coulston, K. J.; Danen, L. B.; Eastwood, F. W.; Irvine, M. J.; Pullin, D. E. *Tetrahedron Lett.* **1986**, *27*, 1075.
(97) Andrews, L.; Dunkin, I. R.; Kelsall, B. J.; Lurito, J. T. *J. Phys. Chem.* **1985**, *89*, 821.
(98) Shida, T.; Momose, T.; Ono, N. *J. Phys. Chem.* **1985**, *89*, 815.
(99) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157.
(100) Marchand, A. P.; Jin, P.-w.; Flippen-Anderson, J. L.; Gilardi, R.; George, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1108.
(101) Herz, W.; Iyer, V. S.; Nair, M. G. *J. Org. Chem.* **1975**, *40*, 3519.
(102) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 2041.
(103) (a) Weinstein, D. I.; Alster, J.; Marchand, A. P. *Thermochim. Acta* **1986**, *99*, 133. (b) Yinon, J.; Bulusu, S. *J. Energet. Mater.* **1986**, *4*, 115.
(104) Marchand, A. P. *Tetrahedron* **1988**, *44*, 2377.
(105) Mehta, G.; Pandey, P. N.; Ho, T.-L. *J. Org. Chem.* **1976**, *41*, 953.
(106) Hirao, K.-i.; Miura, H.; Hoshino, H.; Yonemitsu, O. *Tetrahedron Lett.* **1976**, 3895.
(107) Hirao, K.-i.; Abe, E.; Yonemitsu, O. *Tetrahedron Lett.* **1975**, 4131.
(108) Hirao, K.-i.; Kajikawa, Y.; Yonemitsu, O. *Tetrahedron Lett.* **1977**, 1791.
(109) Hirao, K.-i.; Kajikawa, Y.; Abe, E.; Yonemitsu, O. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1791.
(110) Barborak, J. C.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 1328.
(111) McKennis, J. C.; Brener, L.; Ward, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 4957.
(112) Schmidt, W.; Wilkins, B. T. *Tetrahedron* **1972**, *28*, 5649.
(113) Paquette, L. A.; James, D. R.; Klein, G. *J. Org. Chem.* **1978**, *43*, 1287.
(114) Eaton, P. E.; Or, Y. S.; Branca, S. J.; Shankar, B. K. R. *Tetrahedron* **1986**, *42*, 1621.
(115) Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 2134.
(116) Dauben, W. G.; Cunningham, A. F., Jr. *J. Org. Chem.* **1983**, *48*, 2842.
(117) Eaton, P. E.; Patterson, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 2573.
(118) Prins, H. J. *Recl. Trav. Chim. Pays-Bas* **1946**, *65*, 455.
(119) McBee, E. T.; Roberts, C. W.; Idol, J. D., Jr.; Earle, R. H., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 1511.
(120) For a review, see: Ungnade, H. E.; McBee, E. T. *Chem. Rev.* **1958**, *58*, 249.
(121) McBee, E. T.; Dilling, W. L.; Braendlin, H. P. *J. Org. Chem.* **1962**, *27*, 2704.
(122) Dilling, W. L.; Braendlin, H. P.; McBee, E. T. *Tetrahedron* **1967**, *23*, 1211.
(123) Photolysis of a solution of **164** in cyclohexane or isooctane results in partial reduction, thereby affording a monohydro ($C_{10}HCl_{11}$) and a dihydro ($C_{10}H_2Cl_{10}$) derivative of **164**. See: Alley, E. G.; Dollar, D. A.; Layton, B. R.; Minyard, J. P., Jr.

J. Agric. Food Chem. **1973**, *21*, 138.

(124) Griffin, G. W.; Price, A. K. *J. Org. Chem.* **1964**, *29*, 3192.

(125) Pews, R. G. *Can. J. Chem.* **1969**, *43*, 1260.

(126) Okaya, Y.; Bednowitz, A. *Acta Crystallogr.* **1967**, *22*, 111.

(127) Ungefug, G. A.; McGregor, S. D.; Roberts, C. W. *J. Org. Chem.* **1971**, *36*, 352.

(128) McGregor, S. D.; Roberts, C. W. *J. Org. Chem.* **1970**, *35*, 3576.

(129) Pews, R. G.; Roberts, C. W. *J. Org. Chem.* **1969**, *34*, 2029.

(130) Dilling, W. L.; Dilling, M. L. *Tetrahedron* **1967**, *23*, 1225.

(131) Lehman, T. A.; Harvan, D. J.; Hass, J. R. *Org. Mass Spectrom.* **1980**, *15*, 437.

(132) Marchand, A. P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, p 357.

(133) Godleski, S. A.; Schleyer, P. von R.; Ōsawa, E.; Wipke, W. T. *Prog. Phys. Org. Chem.* **1981**, *13*, 63.

(134) Kent, G. J.; Godleski, S. A.; Ōsawa, E.; Schleyer, P. von R. *J. Org. Chem.* **1977**, *42*, 3852.

(135) The term "stabilomer" is defined as "that isomer possessing the lowest free energy of formation at 25 °C in the gas phase". See footnote 6 in ref 133.

(136) Underwood, G. R.; Ramamoorthy, B. *Tetrahedron Lett.* **1970**, 4125.

(137) Godleski, S. A.; Schleyer, P. von R.; Ōsawa, E.; Kent, G. J. *J. Chem. Soc., Chem. Commun.* **1974**, 976.

(138) (a) Cookson, R. C.; Crundwell, E.; Hudec, J. *Chem. Ind. (London)* **1958**, 1003. (b) Marchand, A. P.; Allen, R. W. *J. Org. Chem.* **1974**, *39*, 1596.

(139) Eaton, P. E.; Hudson, R. A.; Giordano, C. *J. Chem. Soc., Chem. Commun.* **1974**, 978.

(140) (a) Marchand, A. P.; Chou, T.-C.; Barfield, M. *Tetrahedron Lett.* **1975**, 3359. (b) Marchand, A. P.; Chou, T.-C.; Ekstrand, J. D.; van der Helm, D. *J. Org. Chem.* **1976**, *41*, 1438.

(141) Smith, E. C.; Barborak, J. C. *J. Org. Chem.* **1976**, *41*, 1433.

(142) Mehta, G.; Chaudhuri, B. *Indian J. Chem.* **1979**, *17B*, 421.

(143) Helmchen, G.; Staiger, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 116.

(144) Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Org. Chem.* **1978**, *43*, 689.

(145) Naemura, K.; Fujii, T.; Chikamatsu, H. *Chem. Lett.* **1986**, 923.

(146) Dekker, T. G.; Oliver, D. W.; Venter, A. *Tetrahedron Lett.* **1980**, *21*, 3101.

(147) Eaton, P. E.; Leipzig, B. *J. Org. Chem.* **1978**, *43*, 2483.

(148) Nakazaki, M.; Naemura, K. *J. Chem. Soc., Chem. Commun.* **1980**, 911.

(149) Nakazaki, M.; Naemura, K. *J. Org. Chem.* **1981**, *46*, 106.

(150) Nakazaki, M.; Naemura, K.; Hokura, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1245.

(151) Naemura, K.; Hokura, Y.; Nakazaki, M. *Tetrahedron* **1986**, *42*, 1763.

(152) Farina, M.; Morandi, C. *Tetrahedron* **1974**, *30*, 1819.

(153) Fessner, W.-D.; Prinzbach, H. *Tetrahedron* **1986**, *42*, 1797.

(154) Marchand, A. P.; Sharma, G. V. M.; Annapurna, G. S.; Pednekar, P. R. *J. Org. Chem.* **1987**, *52*, 4784.

(155) Nakazaki, M.; Naemura, K.; Hashimoto, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2543.

(156) Nakazaki, M.; Naemura, K.; Nobumasa, A.; Iwasaki, M. *J. Org. Chem.* **1979**, *44*, 2433.

(157) Nakazaki, M.; Naemura, K.; Kondo, Y.; Nakahara, S.; Hashimoto, M. *J. Org. Chem.* **1980**, *45*, 4440.

(158) For a review of the synthesis and chemistry of triblattanes, see: Nakazaki, M.; Naemura, K. *J. Synth. Org. Chem., Jpn.* (*Yuki Gosei Kagaku Kyokai Shi*) **1982**, *40*, 1128.

(159) Sorochinskii, A. E.; Aleksandrov, A. M.; Petrenko, A. E.; Kukhar', V. P. *J. Org. Chem. USSR* (*Engl. Transl.*) **1988**, *23*, 1987.

(160) Petrenko, A. E.; Aleksandrov, A. M.; Sorochinskii, A. E.; Kukhar', V. P. *J. Org. Chem. USSR* (*Engl. Transl.*) **1988**, *23*, 1988.

(161) Tolstikov, G. A.; Lerman, B. M.; Galin, F. Z.; Struchkov, Yu, T.; Andrianov, V. G. *Tetrahedron Lett.* **1978**, 4145.

(162) Aleksandrov, A. M.; Sorochinskii, A. E.; Petrenko, A. E.; Kukhar', V. P. *J. Org. Chem. USSR* (*Engl. Transl.*) **1988**, *24*, 131.

(163) Aleksandrov, A. M.; Sorochinskii, A. E.; Petrenko, A. E.; Kukhar', V. P. *J. Org. Chem. USSR* (*Engl. Transl.*) **1987**, *22*, 681.

(164) Ogino, T.; Awano, K. *Chem. Lett.* **1982**, 891.

(165) Ogino, T.; Awano, K.; Ogihara, T.; Isogai, K. *Tetrahedron Lett.* **1983**, *24*, 2781.

(166) Mehta, G.; Srikrishna, A. *J. Chem. Soc., Chem. Commun.* **1982**, 218.

(167) The crystal structure of **227** has been reported. See: Murthy, G. S.; Venkatesan, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1581.

(168) Mehta, G.; Reddy, A. V.; Tacreiter, W.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 441.

(169) Mehta, G.; Reddy, A. V.; Srikrishna, A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 291.

(170) (a) Harano, K.; Ban, T.; Yasuda, M.; Ōsawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1981**, *103*, 2310. (b) Ōsawa, E.; Ivanov, P. M.; Jaime, C. *J. Org. Chem.* **1983**, *48*, 3990. (c) For a review, see: Ōsawa, E.; Kanematsu, K. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, p 329.

(171) Ogino, T.; Awano, K.; Ogihara, T.; Isogai, K. *Chem. Lett.* **1984**, 2023.

(172) (a) Mehta, G.; Srikrishna, A.; Suri, S. C.; Nair, M. S. *J. Org. Chem.* **1983**, *48*, 5107. (b) Mehta, G.; Rao, K. S.; Marchand, A. P.; Kaya, R. *J. Org. Chem.* **1984**, *49*, 3848.

(173) See: Mehta, G.; Murthy, A. N.; Reddy, D. S.; Reddy, A. V. *J. Am. Chem. Soc.* **1986**, *108*, 3443 and references cited therein.

(174) Ogino, T.; Awano, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2811.

(175) (a) Hamada, T.; Iijima, H.; Yamamoto, T.; Numao, N.; Hirao, K.-i.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1980**, 696. (b) Hamada, T.; Iijima, H.; Yamamoto, T.; Numao, N.; Yonemitsu, O. *Kokagaku Toronkai Koen Yoshishu* **1979**, 2. See: *Chem. Abstr.* **1980**, *93*, 70445*t*.

(176) Herz, W.; Nair, M. G. *J. Am. Chem. Soc.* **1967**, *89*, 5474.

(177) Herz, W.; Nair, M. G. *J. Org. Chem.* **1969**, *34*, 4016.

(178) Herz, W.; Iyer, V. S.; Nair, M. G.; Saltiel, J. *J. Am. Chem. Soc.* **1977**, *99*, 2704.

(179) Naemura, K.; Katoh, T.; Chikamatsu, H.; Nakazaki, M. *Chem. Lett.* **1984**, 1371.

(180) Tezuka, T.; Yamashita, Y.; Mukai, T. *J. Am. Chem. Soc.* **1976**, *98*, 6051.

(181) (a) Marchand, A. P.; Zhao, D., unpublished results. (b) The structure of pentacyclo[$5.4.0.0^{2,5}.0^{3,10}.0^{4,8}$]undecane-10-carboxylic acid (i.e., the carboxylic acid derived via Wolff–Kishner reduction of keto ester **281** followed by aqueous acidic workup) has been elucidated by single-crystal X-ray crystallographic analysis. Watson, W. H.; Kashyap, R.; Marchand, A. P.; Zhao, D.; Vidyasagar, V., unpublished results.