Acknowledgments. Financial support from the National Institutes of Health (Grants AM-04257 and RR 00612-05A1) is gratefully acknowledged. We also thank the proprietor of the SMIP Shorthorn Ranch (Woodside, Calif.) for facilitating the plant collection on his ranch.

Registry No.—**1** HCl, 18017-52-2; **2**, 494-15-5; **3**, 52196-10-8; **4**, 52195-93-4; **5**, 494-52-0; **6**, 24380-92-5; **7**, 40199-45-9; **8**, 486-70-4; **9**, 52196-11-9; **13**, 52195-94-5; **14**, 52196-12-0; **16**, 52195-95-6; **18**, 52195-96-7; **20a**, 23972-23-8; **20b**, 23972-24-9; **24**, 52196-13-1; **25**, 52196-14-2.

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Diamantane. I.[1] Preparation of Diamantane. Physical and Spectral Properties

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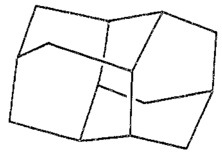
The preparation of diamantane (I) by Lewis acid catalyzed rearrangements of various pentacyclic tetradecanes has been examined. The best yield (84%) was obtained from *trans*-tetrahydro-Binor-S (XXXV). However, the most convenient synthetic procedure involves rearrangement of hydrogenated Binor-S (XXVII/XXVIII), which gives I in ~70% yield. Other more highly strained precursors give I in lower yield (1–47%) owing to disproportionation. The diamond lattice structure of diamantane, confirmed by X-ray analysis, is consistent with high thermodynamic stability. However, I, like adamantane, is not strain free. Molecular mechanics calculations show that this is due to an excess of repulsive over attractive nonbonded interactions in comparison with noncage hydrocarbons. The spectral properties of diamantane are characterized by a single-line proton nmr spectrum, resistance toward mass spectral fragmentation, and a simplified ir spectrum due to high symmetry.

The beautiful three-dimensional array of the diamond lattice has provided many structural insights and synthetic challenges.[3–5] Prelog[4] recognized that cyclodecane in conformation II is such a diamond lattice hydrocarbon and can be deduced from the pentacyclotetradecane I by replacing two CH and two CH_2 by six hydrogens.[6,7] At Prelog's suggestion, I (pentacyclo[$7.3.1.1^{4,12}.0^{2,7}.0^{6,11}$]tetradecane) was chosen as the Congress Emblem of the 1963 London IUPAC meeting, and was featured as a decoration on the cover of abstracts, program, and publicity material. The *Handbook* challenged the Congress participants to synthesize I, and this challenge was reiterated by Cram and Hammond on the end papers of their popular text.[4c] The first preparation of "Congressane" was achieved at Princeton in 1965 in 1% yield by aluminum halide catalyzed isomerization of a mixture of norbornene [2 + 2] photodimers.[8]

Adamantane (IV) is the first and "Congressane" only the second member of an entire family of compounds "whose ultimate is diamond."[7] The synthesis of the third member of the series (V) in 1966[9] emphasized the need for a more general scheme of semitrivial nomenclature. Following the suggestion of Vogl and Anderson,[7] I was renamed "diamantane" and V designated triamantane.[7] The synthesis of tetramantane (three isomers are possible)[10] and of higher "amantanes" has not yet been achieved.

The year 1966 also marked the isolation of diamantane (I) from the high-boiling fractions of the crude oil of Hodonin (from which adamantane was discovered)[11] and the



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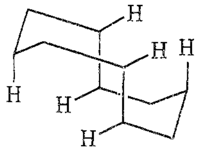
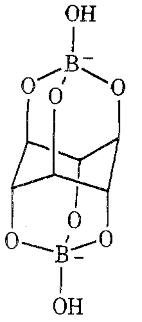
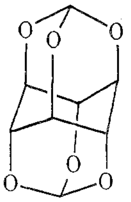


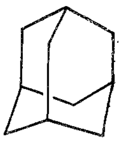
II



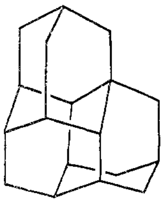
IIIa



IIIb



IV



V

achievement of a significant improvement in the yield of I (to 10%) by rearrangement.[2c] While this permitted a start to be made in the exploration of the chemistry of diamantane, the hydrocarbon was still difficult to obtain in quantity.

Subsequent work at Princeton explored various alternative precursors for diamantane with increasing success and culminated in a truly convenient high-yield preparation, reported in preliminary form in 1970.[12] Diamantane then became as readily available as adamantane and the chemistry of I could be studied easily. McKervey developed similar preparative improvements; a full report was published in 1972.[13a]

We recount here the preparative studies which led to a convenient synthesis, and summarize the physical properties of diamantane. The following two papers describe the chemical behavior and the functionalization of diamantane. The detailed analysis of the mechanisms of the rearrangements leading to diamantane from various precursors will be published separately.[1e]

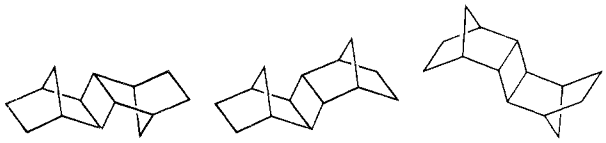
Results and Discussion

Preparation. A convenient preparation of adamantane was achieved in 1956[14] by aluminum halide catalyzed isomerization of the tricyclic $C_{10}H_{16}$ *endo*-tetrahydrodicyclopentadiene.[3,14] Subsequently, it was found that many saturated tricyclic hydrocarbons with ten or more carbon atoms rearrange to the thermodynamically most stable adamantane isomers.[3,14] The generality of these rearrangements suggested that the relatively unstrained diamantane might be obtained by isomerization of pentacyclic $C_{14}H_{20}$ hydrocarbons.

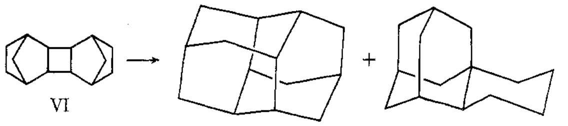
The first $C_{14}H_{20}$ isomers investigated were pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes, represented by general structure VI (Chart I). Three stereoisomers are now known (VIa–c), and are readily available either by dimerization of norbornene or by hydrogenation of the [2 + 2]-type norbornadiene dimers.[15,16]

Rearrangement of the photodimers of norbornene[15] prepared from acetone-sensitized dimerization[15] (consisting of 12% *exo-trans-exo*-VIa and 88% *endo-trans-exo*-VIb) with $AlCl_3$ gave diamantane in 1% yield.[8] Although the reaction mixture was complex, containing besides tar many fragmentation and disproportionation products, isolation of diamantane (I) was facilitated by its high insolubility and crystallinity.

Chart I



	VIa exo-trans-exo	VIb endo-trans-exo	VIc endo-trans-endo
$\Delta H_f°$, gas, 25° (calcd)	9.56 kcal/mol	14.51	19.97[a]
strain (calcd),	57.62 kcal/mol	62.57	68.03[a]



VI I VII

[a] Close to final value (within 0.3 kcal/mol).

Lewis acid catalyzed treatment of strained hydrocarbons often does not give very satisfactory yields of isomerization products.[3] The reason appears to be that excessive strain encourages an alternative mode of strain relief: ring cleavage *via* protonation, followed by disproportionation to give olefin and alkane with one less ring. The former polymerizes to tar under the reaction conditions. It is not difficult to see why VI, a combination of strained norbornane and cyclobutane units, should be especially prone toward disproportionation.

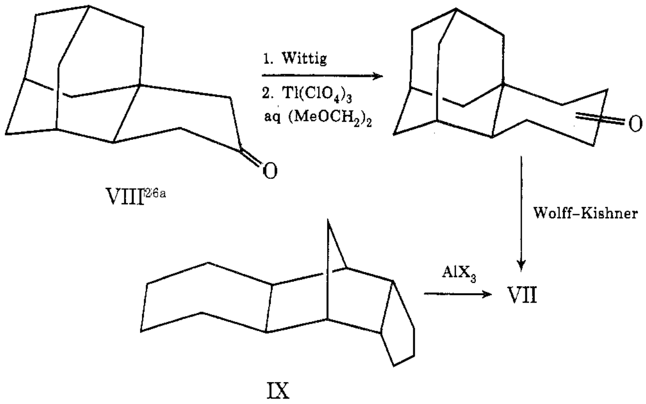
Variation of temperature, concentration, and solvent did not improve yields significantly. Use of a better precursor was indicated. Since the major component of the original mixture was the more strained VIb,[15,17] it was hoped that VIa,[15] available by cuprous chloride sensitized photolysis of norbornene, would give less disproportionation and a better yield of I. However, only a 2% yield was achieved with $AlCl_3$.

Schneider[18] showed that a "sludge" catalyst, prepared by cracking low molecular weight branched hydrocarbons with an aluminum halide and HX, gave improved yields of substituted adamantanes from perhydrogenated tricyclic aromatic compounds. At Princeton,[2c] a similar "sludge" catalyst system was prepared by adding *tert*-butyl bromide to a suspension of aluminum bromide in cyclohexane. Like the Schneider catalyst,[18] this $AlBr_3$ "sludge" is a yellow, heavy oil possessing an internal initiator and may be stored for longer periods of time under cyclohexane. Activity may be augmented or regenerated by addition of small amounts of $AlBr_3$. The actual composition of the catalyst is not known, but probably consists of polymerized isobutane, formed by elimination of HBr from *tert*-butyl bromide.[2c,18–21] "Sludge" catalysts may also be prepared from *sec*-butyl bromide or from *tert*-butyl chloride with $AlCl_3$.[22]

The activity of "sludge" catalyst was tested first with *endo*-tetrahydrodicyclopentadiene and improved yields of adamantane were obtained.[2c] Robinson and Tarrat[23] subsequently prepared a similar *tert*-butyl bromide catalyst and confirmed its greater efficiency. Yields of adamantane as high as 66% from *endo*-tetrahydrodicyclopentadiene and improved yields of alkyl adamantanes were reported.[23,24]

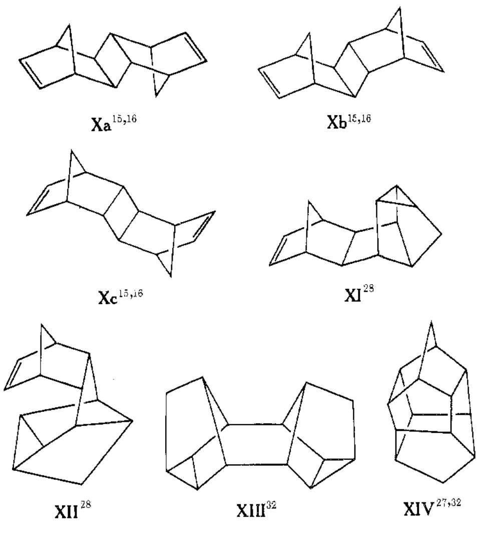
The rearrangements of the isomeric pentacyclic [8.2.1.1.^{4,7}.0^{2,8}.0^{3,9}]tetradecanes (VI) were reinvestigated with the more active "sludge" catalyst. Significant improvement was achieved. However, the best yield obtained from any of these [2 + 2] dimers was still only ~11%, and this was from the least strained exo-trans-exo isomer (VIa). Sludge catalyst isomerization of hydrogenated commercial norbornadiene dimer (a mixture of 26% VIa, 71% VIb, and 3% VIc) gives diamantane in not more than 5% yield.

While the yields of diamantane (I) were low from all isomers of VI, a tetracyclic $C_{14}H_{22}$ disproportionation product (VII) was always the major product (yields up to 40%).[25] The structure of this product was initially assigned on the expectation that it should be the most stable $C_{14}H_{22}$ isomer.[17] This assignment has been verified recently; VII is identical in glc retention times, nmr, and ir with a sample prepared unambiguously from VIII.[26a] VII is also identical with the main product of rearrangement of IX, an isomeric starting material with quite a different structure.[26b]



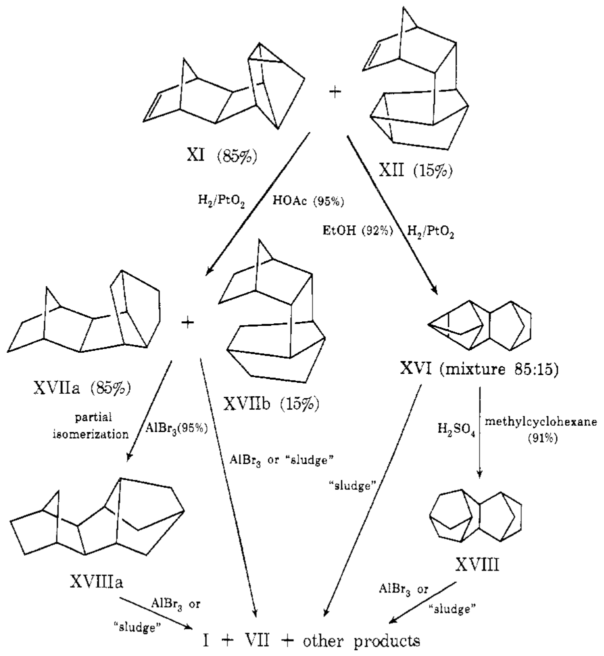
Isomerization of Hydrogenated Katz Dimer. All the [2 + 2] dimers of norbornene (VI) and norbornadiene (X) contain a strained cyclobutane ring which favors disproportionation. Consequently, less strained precursors were sought. Norbornadiene is readily dimerized by various organometallic catalysts.[27,28] Of the seven known dimers[27] (Chart II), three are of the [2 + 2] type (Xa–c),[15,16] two [4 + 2] incorporate one nortricyclene unit (XI, XII),[28] and one [4 + 4] type (XIII) contains two fused nortricyclene units; a cage structure (XIV)[27] completes the list.

Chart II
Known Norbornadiene Dimers



The Katz[28] norbornadiene dimers, consisting of a 7:1 mixture of XI and XII, were obtained from norbornadiene using rhodium/carbon catalyst.[28] Only the double bond hydrogenated under most of the conditions tried, which included even use of Ni catalyst and high pressures. Isomerization of the resulting hexacyclic mixture XVI with sludge catalyst (Scheme I) gave diamantane in up to 16% yield (glc). This result *depended on* disproportionation; in addition, the double disproportionation product (VII) formed in substantial amounts.

Scheme I



Catalytic hydrogenation of the mixture XI and XII in acetic acid with PtO_2 catalyst[29,30] succeeded in reducing both the double bond and the cyclopropane ring to produce two pentacyclic isomers in a 85:15 ratio. By analogy with results of hydrogenation of Binor-S (XIII) and deltacyclane (see later) under similar conditions, structures XVIIa and XVIIb were assigned, the former arising from XI and the latter from XII. Reduction of partially hydrogenated mixture XVI by hydride transfer in concentrated sulfuric acid–methylcyclohexane[31] also gave, in 91% yield, an 85:15 ratio mixture of two cyclopropane cleaved pentacyclic isomers. These differed from XVIIa and XVIIb and were assigned general structure XVIII. A ^{13}C nmr proton decoupled spectrum of the major isomer indicated nine different carbon absorptions and is consistent with structure XVIIIa. Although three other isomers in the set would fit the ^{13}C nmr data, XVIIIa is the lowest energy isomer (see below).

Isomerization of either mixture XVII or XVIII, with aluminum bromide or with sludge catalyst, gave diamantane in up to 25% yields (Table I).

Interestingly XVIIIa appears to be identical with the rearrangement intermediate isolated when AlX_3 isomerization of mixture XVII was interrupted after partial reaction. Such reactions are followed conveniently by gas chromatography. In this way, we demonstrated that intermediate XVIIIa forms diamantane in a yield identical with that from mixture XVIII. Apparently, sulfuric acid effected a similar partial isomerization in giving XVIII.[31]

Courtney, Johnston, McKervey, and Rooney also hydrogenated Katz dimer (XI and XII) in acetic acid and obtained a cyclopropyl-cleaved product which could be isomerized in the gas phase to diamantane in 45% yield employing a chlorinated platinum–alumina catalyst.[13a]

Although the yield it gives is an improvement over that from the [2 + 2] dimers, Katz dimer is not ideal as a diamantane precursor. Examination of the glc trace of a crude $AlBr_3$ isomerized mixture of XVII or XVIII reveals at least 14 products besides diamantane, including a major amount of disproportionation product VII, and other fragmentation products. Furthermore, we have had difficulty

Table I
C_{14} Pentacyclic Precursors Investigated in the Preparation of Diamantane

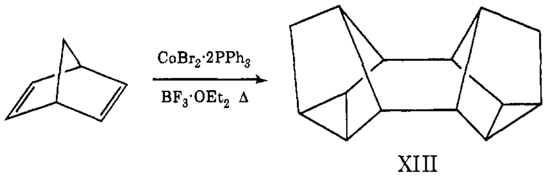
Precursor	Registry no.	Catalyst	% yield diamantane (I)	Ref
VI (12% VIa)	1624-14-2	$AlCl_3$	1	8, *a*
(88% VIb)	1624-16-4	"Sludge"	1–5	
VIa		$AlCl_3$	2	2c
		"Sludge"	10	
XVI	51966-13-3	"Sludge"	10–16	*b*
XVII	51966-14-4	$AlBr_3$	25	*c*
		"Sludge"	20	*c*
		Pt/Cl/alumina	45	13
XVIII	51966-15-5	$AlBr_3$	25	*c*
		"Sludge"	18	
XXI	51982-54-8	"Sludge"	41–47	12
XXIV	51982-55-9	"Sludge"	25	12
XIII	13002-57-8	"Sludge"	10	*c*
		H_2SO_3	30	*c*, 13
XXVII/XXVIII		$AlBr_3$	62–75	12
		"Sludge"	71	12
		$AlCl_3/CH_2Cl_2$	70–90	13
XXXV	51966-16-6	$AlBr_3$	84	*c*

[a] S. Halá, J. Novák, and S. Landa, *Sb. Vys. Chem.-Technol. Praze, Technol. Paliv*, **19,** 9 (1969). [b] Reaction carried out by Dr. Leo Lam. [c] This work.

in obtaining good yields of Katz dimer. The reaction is highly erratic; yields ranged from 0 to 49% and were found to be dependent on the catalyst quality and other unknown factors.

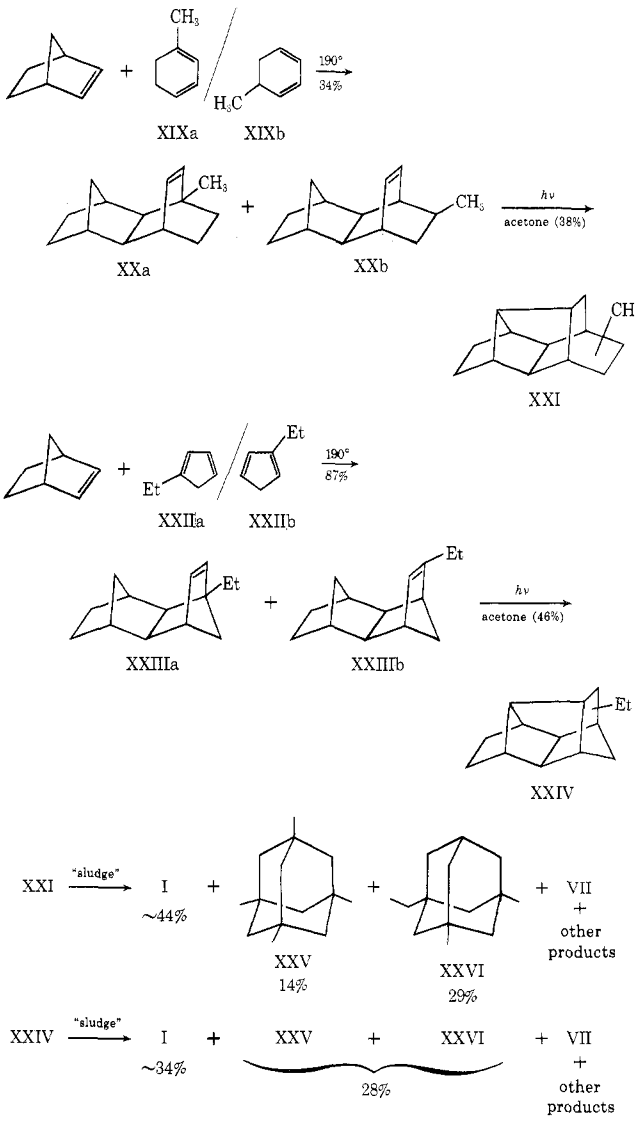
Diamantane from Other Precursors. In our search for other precursors, pentacyclic hydrocarbons XXI and XXIV were prepared as shown in Scheme II. These gave diamantane in 44 and 34% average yields, respectively, upon rearrangement with sludge catalyst (Table I). While diamantane was the *main* product, 1,3,5,7-tetramethyladamantane (XXV)[18] and 1,3-dimethyl-5-ethyladamantane (XXVI)[18] were identified as components of the reaction mixture. VII and other unidentified products were present in smaller amounts. Although these rearrangements give somewhat better yields of diamantane, the starting materials are cumbersome to prepare and the routes are not convenient.

Diamantane from Hydrogenated Binor-S. The availability *in almost quantitative yield of a* [4 + 4] *norbornadiene* dimer, "Binor-S" (heptacyclo[8.4.0.$0^{2,12}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$.$0^{11,13}$]tetradecane, XIII)[27,32] afforded an ideally constituted precursor, especially since the cyclopropane rings can be reduced to give a $C_{14}H_{20}$ pentacyclic hydrocarbon.



XIII

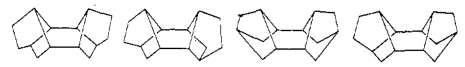
Scheme II



Hydrogenation of Binor-S. Schrauzer[32] has reported that the hydrogenation of Binor-S at 200° with 305 atm hydrogen pressure and Pt catalyst gave a mixture of products consisting of 94% $C_{14}H_{20}$, and 6% $C_{14}H_{18}$ hydrocarbons. The solvent was not indicated, however. We have found that Binor-S did not take up hydrogen in acetic anhydride, even under 102 atm hydrogen pressure with PtO_2 catalyst. However, in agreement with our earlier experience,[29,30] the cyclopropyl rings in Binor-S were readily cleaved by hydrogenation in glacial acetic acid with PtO_2 catalyst.[12] The resulting liquid product [bp 105–110° (1.5 mm)] appears by gas chromatographic analysis on numerous columns to be essentially one material. Cleavage of both cyclopropane rings was confirmed by nmr analysis, which indicated absence of nortricyclene peaks at δ 1.05 and the presence of a more complicated spectrum with peaks in the δ 2.25–0.75 region. These results were verified by McKervey.[13a]

Hydrogenation of Binor-S may, in principle, give rise to four tetrahydro-Binor-S isomers (XXVII–XXX) from the

Table II
Possible Hydrogenation Products of Binor-S,[a,b] Point Group Classifications and Calculated Heats of Formation



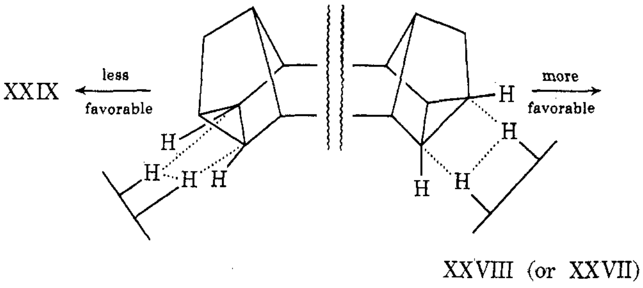
	XXVII (51966-17-7)	XXVIII (51966-18-8)	XXIX (52021-70-0)	XXX (51966-19-9)
Point group	C_s	C_2	C_{2h}	C_i
Number of different carbon atoms	7	7	5	14
$\Delta H_f°$, gas, 25° (calcd),[c] kcal/mol	14.10	6.09	1.55	2.27
Strain (calcd),[c] kcal/mol	62.16	54.15	49.61	50.33

[a] References 31-33. [b] Registry numbers in parentheses. [c] Reference 17.

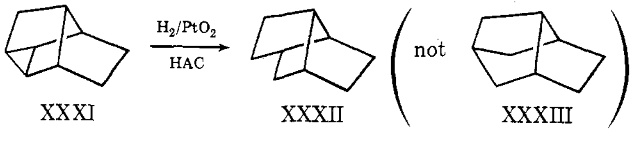
various possible cyclopropane ring reductions (Table II). Hydrogenolysis of unactivated cyclopropane rings usually results in the cleavage of the least substituted cyclopropyl ring bonds.[29-31,33] However, in XIII, all cyclopropane bonds are disubstituted. In such strained molecules, hydrogenolysis of the most strained bond seems from literature examples[31] to be a reasonable expectation.

Molecular mechanics calculations showed that XXIX and XXX should be the most stable isomers.[17] However, ^{13}C nmr spectroscopy[34] of the reduction product eliminated these structures from contention, since six signals for seven carbons were observed, there being one coincidence of chemical shift in the single frequency off resonance and noise resonance decoupled spectra. The sharpness of peaks indicated that only one isomer was present. Isomer XXX, possessing no symmetry, should give a 14-line spectrum, whereas the more symmetrical XXIX has only five different kinds of carbon atoms. It is difficult to differentiate between XXVII and XXVIII by ^{13}C nmr, since both isomers possess seven unique carbons of the same general type. A choice may ultimately be possible between the two structures, since XXVIII is chiral while XXVII is not. If strain relief during reduction is a factor, XXVIII should be favored over XXVII on the basis of the molecular mechanics calculations, and we tentatively assign the structure on this basis.

The reduction of XIII to give XXVIII (or XXVII) and not XXIX or XXX is probably influenced by steric interaction during approach of catalyst-bound hydrogen. Other systems containing nortricyclene units behave similarly. For example, deltacyclane (XXXI) gives brexane (XXXII).[31,35] On this basis, we assigned structures XVII to the hydrogenated Katz dimers.



XXVIII (or XXVII)



XXXI XXXII XXXIII

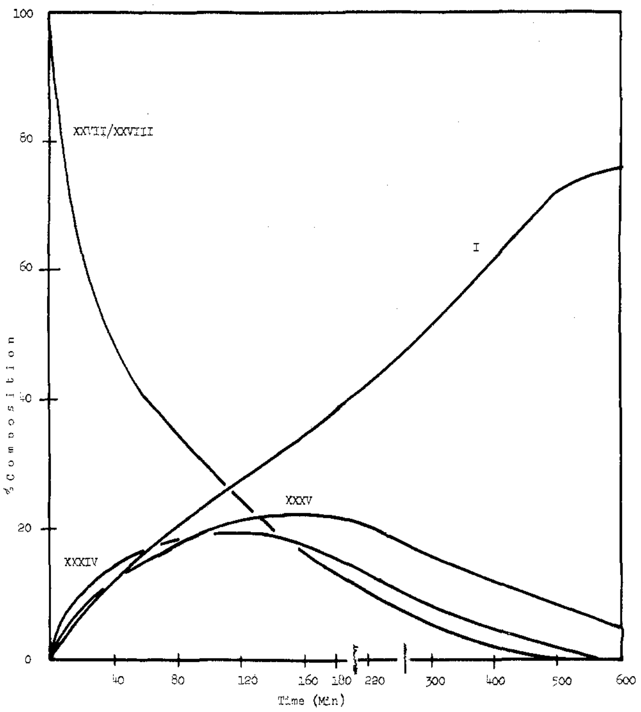
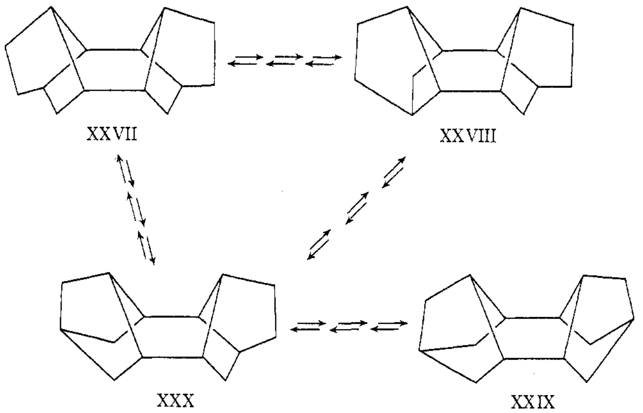


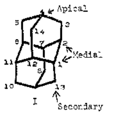
Figure 1. Isomerization of tetrahydro-Binor-S (XXVII/XXVIII) to diamantane (I) at 25° with aluminum bromide in cyclohexane.

Isomers XXVII and XXVIII may be interconverted by simple Wanger-Meerwein 1,2 shifts; either should give diamantane by further rearrangement. In fact, all the tetrahydro-Binor-S type isomers (XXVII-XXX) are, in principle, interconvertible by such 1,2 shifts (the intermediate cations can be generated by hydride abstraction).

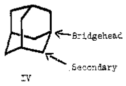


Rearrangement of Tetrahydro-Binor-S. The aluminum bromide or "sludge" catalyzed isomerization of tetrahydro-Binor-S in either carbon disulfide or cyclohexane proceeds smoothly and quickly. Careful glc study of the course of the reaction at 0 and 25° indicates that isomerization proceeds with formation of at least two major, and several minor (less than 1%), intermediates. At the end of the reaction, however, only diamantane (over 90% of the product) and tetracyclic disproportionation product VII remain. At 0°, an as yet unidentified $C_{14}H_{20}$ intermediate (XXXIV) is formed initially; this then isomerizes to the major intermediate, which was isolated and could be identified as *trans*-pentacyclo[8.2.1.1.^{2,5}.0^{3,7}.0^{8,12}]tetradecane (XXXV). The concentration of XXXV builds up to a maximum value of over 20%; after several hours, rearrangement proceeds further to form diamantane and VII. Figure 1, a

Structural and Physical Properties. The lower symmetry of diamantane (I) (D_{3d}) compared to adamantane (IV) (T_d) is reflected in its lower melting point (251°[15] vs. 268-269°, Table IV) and in its greater structural complexity. Thus, I possesses not one, but two types of bridgehead positions, designated "medial"[38] (C-1,2,6,7,11,12) and "apical" (C-4 and 9). The six methylene groups in I are equivalent but, unlike those of adamantane, are prochiral. However, despite the three types of hydrogens, the 100 MHz proton nmr spectrum of I consists of a single relatively sharp signal (δ ~ 1.68) whereas that of IV exhibits two partially separated signals (δ ~ 1.78). At 220 MHz, IV displays a cleanly separated two line spectrum (δ 1.87 and 1.74 ppm)[37] due to the two types of hydrogens, whereas I still gives only a singlet broadened at the base. The ^{13}C-nmr spectra of



I



IV

I[36] and IV[39] are straightforward, consisting of three and two lines, respectively (Table IV). The ir and Raman spectra of I and IV are quite simple, indicating a high degree of symmetry (Table IV).

The mass spectrum of diamantane (I)[8] shows even less fragmentation than that of adamantane (IV)[39,40] (Table IV). This behavior is due to the interlocking cage framework. As in the case of IV (M+, m/e 136),[40] the parent ion of I (m/e 188)[8] is the most intense but by more than a factor of three than any other peak in the spectrum. Such prominent parent ions are formed from other multicyclic cage molecules such as ethanoadamantane (m/e 162),[11] ethanodiamantane (both isomers) (m/e 214),[41] triamantane

(m/e 240),[9] bastardane (m/e 292),[10] homoadamantane (m/e 150)[42] etc.; the inherent stability of such molecular frameworks resist fragmentation. Some exceptions in cage molecules have been noted. Noradamantane[38a,b,i] exhibits its base peak at m/e 80 (molecular ion 122), and other strong peaks are present.

The second most intense peak in I, $C_7H_7^+$ (m/e 91), seems characteristic of many diamondoid and cage molecules and is also prominent in ethanoadamantane,[11] ethanodiamantane,[41] triamantane,[9] bastardane,[10] etc. Similar cage molecules, e.g. adamantane[3,40] and homoadamantane[42] exhibit the second most intense peak at m/e 93. In general, both diamantane and adamantane are resistant towards loss of one carbon fragments, while two and especially three and four carbon losses are somewhat more facile.

X-ray analyses of diamantane (I)[43] and adamantane (IV) confirm the expected similarities of these diamond lattice structures: C-C bond lengths ~ 1.54 Å, 60° dihedral angles, and approximately tetrahedral (109.5 ± 1.5°) bond angles (Table IV). These near ideal features are reflected by the high thermodynamic stability of these hydrocarbons; adamantane is the most stable substance of empirical formula $C_{10}H_{16}$ and diamantane is the most stable $C_{14}H_{20}$ structure possible. Despite these favorable features, both adamantane and diamantane are not strain free (Table V). An initial strain estimate based on an experimental heat of formation (ΔH_f°, gas, 25°) of -32.96 ± 0.19 kcal/mole,[44] and a "strain free" group increment scheme indicated a strain of 6.48 kcal/mole for adamantane.[45] Since then, two new determinations of ΔH_f° have been reported, -30.65 ± 0.98[46] and -30.57 ± 0.9 kcal/mole.[47] Both differ from the original and indicate a higher strain energy of 8.85 kcal/mole. An initial strain estimate for diamantane (I) of 8.49 kcal/mole, based on an experimental heat of formation (ΔH_f° gas, 25°) of -39.55 ± 2.0

kcal/mole,[48] suggested that I was strained to approximately the same extent as IV. However, the discovery of two solid-solid phase transitions in I resulted in a corrected heat of formation of -36.64 kcal/mole,[49] raising the total strain energy to 11.42 kcal/mole. Diamantane is thus indicated to be more strained than adamantane but interestingly the strain per carbon seems to be nearly constant (0.8 - 0.9 kcal/mole).

Molecular mechanics calculations[17,45,50] have been employed to determine the origin of the strain in both systems. Calculations by Schleyer, et al.[45] suggested that the strain could be accounted for mainly in terms of C....C non-bonded repulsions. Allinger, et al.[50] came to a different conclusion, attributing the strain to an excessive number of H...H repulsions. While the use of different non-bonded potential functions are responsible for the different interpretations,[17b,50] both calculations agree in their estimated heats of formation and predict diamantane to be more strained than adamantane (Table V).

It is interesting that I and IV violate the conventional principles of conformational analysis which predict these diamond molecules to be strain free. In cage structures, the blend of repulsive and attractive non-bonded interactions is different from that found in acyclic, monocyclic or condensed polycyclic compounds; the repulsive terms became realtively more important in I and IV. It is probably significant in this context that diamond has rather exceptionally long C-C bonds, 1.5445 Å,[51] and actually is less stable than graphite.[51]

TABLE IV. COMPARISON OF STRUCTURAL AND PHYSICAL PROPERTIES OF DIAMANTANE AND ADAMANTANE

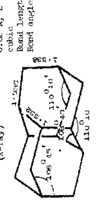
	Diamantane	Ref	Adamantane	Ref
Melting Point	244-245.4°, 251°	12, 15	268-269°	a, 14
H-1 Nmr (δ)	1.68 (s) (w_h=3Hz)	8	1.78, 1.74 (d, J ≅ 1.7 Hz) 1.87, 1.74 (two signals due to methine and methylene, 220 MHz)	37
^{13}C-Nmr (δ)[b]	38.47 (medial), 37.76 (secondary), 26.18 (apical)	38	28.6 (bridgehead), 38.0 (methylene)	39
IR (cm^{-1})	2908, 2878, 2851, 1442, 1457, 1047 (w)	8	2907, 2933, 2857, 1455, 1357, 1155, 799, 966, 714	c
Raman (cm^{-1})	2926, 2907, 2880, 2851, 1444, 1308, 1233, 1179, 1086, 1072, 1039, 982, 935, 708	8	2944, 2917, 2895, 2849, 1437, 1315, 1223, 1099, 972, 951, 760, 443	3c
Mass spectrum	188 (M^+) (100), 160 (5), 159 (10), 145 (7.5), 131 (12.5), 130 (17.5), 120 (7.5), 105 (15), 91 (C_7H_7,28), 79 (25), 67 (10).	8, 15	136 (M^+) (100), 121, 107, 93 (49), 91 (8), 80 (37) 79 (48) 67	3c, 40
Structure (X-ray)  	Space group-Pa3, a-10.109 ± 0.02 Å, Z-4, ρ = 1.210 g/cm³, cubic Bond lengths (± 0.005 Å, see figure) Bond angles ± 25'	43	Space group-Td^2Fm^3m, a-9.426 ± 0.008 Å, ρ = 1.07 g/cm³, cubic Bond lengths C-C = 1.54 ± 0.01 Å Bond angles 109.5 ± 1.5°	d

TABLE IV cont.

[a] S. Landa and V. Machacek, Collection Czech. Commun., 5, 1 (1953). [b] Ppm from tetramethylsilane. [c] R. Mecke and H. Spiesecke, Ber., 88, 1997 (1955). [d] J. Donohue and S.H. Goodman, Acta Crystallogr., 22, 352 (1967); cf. C.E. Nordman and D.L. Schmitkons, ibid., 18, 764 (1965).

TABLE V EXPERIMENTAL AND CALCULATED ENTHALPIES AND STRAIN ENERGIES OF ADAMANTANE AND DIAMANTANE

	ΔH_f° (gas, 25°, kcal/mole)			Strain energy (gas, 25°, kcal/mole)		
		Calcd			Calcd[c]	
	Exptl	Engler Force Field[a]	Allinger Force Field[b]	Exptl	Engler Force Field[a]	Allinger Force Field[b]
Adamantane	-32.96[44] -30.65[46] -30.57[47]	-32.50	-33.79	6.48 8.85	6.87	6.81
Diamantane	(-39.55)[48,d] -36.64[49]	-37.37	-38.04	(8.49)[d] 11.42	10.69	10.34

[a] Reference 17. [b] Reference 50. [c] Calculated from strain free group increments, cf. ref 45. [d] Superseded values, see text.

Experimental Section

Microanalyses were performed at Hoffmann-La Roche, Inc., Nutley, N.J., and by Robertson Laboratories, Florham Park, N.J. Infrared spectra were determined either in KBr pellets or as nujol mulls using a Perkin Elmer 237 or 631 spectrophotometer. Nmr spectra were recorded on Varian A-60A and HA-100 spectrometers. Chemical shifts are reported in units of δ (ppm) relative to internal tetramethyl silane. Gas chromatographic analysis and separations were performed on either a Varian Aerograph 90-P instrument or on a Perkin Elmer 810 gas chromatograph. Melting points were taken on a Mettler FP1 apparatus, or in an oil bath, and are not corrected.

Preparation of Precursors. Cobalt dibromide-triphenyl phosphine ($CoBr_2 \cdot 2P\phi_3$ Catalyst.[32a,b] Benzene (200 ml), containing 10 g (0.046 mole) anhydrous cobalt dibromide (ROC/RIC) and 24.4 g (0.092 mole) triphenyl phosphine, was refluxed until a color change from green to blue-green occurred. The blue-green catalyst precipitated upon cooling to room temperature in nearly quantitative yield.

Binor-S (XIII)[32] The procedure of Schrauzer[32] with minor modifications was followed. A 1 liter 3 necked flask equipped with teflon sleeves, two efficient high capacity condensers and a mechanical stirrer, was flushed with N_2 and charged with 200 g of freshly distilled norbornadiene. Then 2.0 g $CoBr_2 \cdot 2P\phi_3$ catalyst (see above) and 5 ml of BF_3-etherate (Eastman, distilled within two weeks and kept in the cold) co-catalyst were added. The reaction mixture was heated to 90° until reflux commenced. At this point, the heating mantle was removed as a vigorous exothermic process ensued. This exothermic process must be allowed to proceed as rapidly as possible; only occasional cooling (dry-ice acetone) is desirable (too much cooling results in unwanted polymer formation). After the exothermic process subsided

(5-10 minutes), the brownish-green mixture was allowed to cool to room temperature. Workup included addition of about 100 ml methylene chloride and washing with a saturated sodium bicarbonate solution and with water (~ 100 ml). The methylene chloride solution was dried over $MgSO_4$ and evaporated under reduced pressure to give 164-190 g (86-95%) of low melting solid, mp 59-60°. Distillation (bp 90°/1.5 mm) gave upon cooling 160-170 g (80-85% yield) of a white solid, mp 63-64° (lit.[27] 65-66°).

The reaction may also be carried out in hot toluene as suggested by McKervey.[13a] This avoids the overly vigorous reaction.[12]

Tetrahydro-Binor-S (XXVII/XXVIII) by Catalytic Hydrogenation of Binor-S in Acetic Acid. Binor-S (236 g, 0.78 mole) was partially dissolved in hot glacial acetic acid (900 ml) containing 10 ml conc. HCl; PtO_2 (1.5 g) catalyst was added and the mixture was shaken in a Parr apparatus under 3 atm hydrogen pressure for three hours at 70°. After cooling to room temperature, the catalyst was filtered, water was added, the top layer was separated, and the bottom layer extracted with methylene chloride. The combined organic layers were washed with water, dried, and evaporated. The crude tetrahydro-Binor-S was further purified by distillation under reduced pressure, bp 105-110° (1.5 mm), to give 212-231 g (90-97%) of a colorless liquid; glc (15% Apiezon L, 6m X 3mm column, 200°) indicated mainly one peak. Small amounts (< 1%) of other products were present. Sometimes fractions of bp above 130° are obtained when heating is prolonged during distillation. The rearrangement to diamantane is generally carried out using the middle fraction, which appears to be essentially one isomer (XXVII or XXVIII); mass spectrum m/e (rel intensity) 188 (M^+) (100), 173, 159, 147, 146, 145 (51), 134, 133, 131, 119, 105, 93, 92, 91 (55), 80, 79 (4), 77, 67; nmr

($CDCl_3$) complex spectrum in the range δ 2.25-0.75 and absence of cyclopropyl protons at δ1.05; ^{13}C nmr (ppm from TMS) 49.3 $(CH)_2$, 39.0 $(CH)_2$, 37.5 $(CH)_2$, 36.7 $(CH)_2$, 31.9 $(CH_2)_4$, 27.5 $(CH_2)_2$.[34] This compound has also been prepared and characterized by McKervey.[13]

Trans-Pentacyclo[8.2.1.1.^{2,5}.0^{3,7}.0^{8,12}]tetradecane (XXXV) from Binor-S in Sulfuric Acid-Methylcyclohexane. To 50 ml of 97% sulfuric acid was added dropwise with cooling and stirring 20.0 g Binor-S dissolved in 100 ml methylcyclohexane. A color change from yellow to red was observed and after 1/2 hour, and methylcyclohexane layer was separated. The acid layer was further extracted with methylcyclohexane and the combined organic layers were washed with water, dried over $MgSO_4$ and evaporated. A residue, a combination of oil and solid, was obtained (17.6 g); glc (10% carbowax, 20 M, 3 m x 3 mm column, 170°) indicated four peaks with retention times 10 min (34%), 11.5 min (51%), 12.8 min (5%), and 13.9 min (6%) corresponding to XXXVI (structure undetermined), trans-pentacyclo[8.2.1.1^{2,5}.0^{3,7}.0^{8,12}]tetradecane (XXXV), diamantane (I), and unreacted Binor-S (XIII). XXXV was isolated from the reaction mixture by recrystallization from petroleum ether (60-70°)/acetone, white crystals, mp 111-112° were obtained; mass spectrum m/e (rel intensity) 188 (M^+) (100), 173, 159, 147, 146, 145, 134, 133, 132, 131, 119, 117, 105, 93, 92, 91, 79, 67; nmr (CCl_4) δ 1.0 (d, J ≅ 10 Hz, 3H), 1.4 (s, 5H) 1.7 (m, 2H), 2.1 (d, br, J ≅ 10 Hz); ^{13}C-nmr (CCl_4, ppm from TMS) 40.1 $(CH_2)_2$, 37.8 $(CH)_2$, 37.5 $(CH)_4$, 35.4 $(CH_2)_4$, 33.2 $(CH)_2$.

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.50, H, 10.70.

Reaction at room temperature produces the same four compounds in the following ratios: XXXVI (36.5%), XXXV (37.6%), diamantane (15%) and unreacted Binor-S (3%). A portion (1.82 g) of this mixture gave diamantane in 70% yield upon rearrangement with $AlBr_3$ in cyclohexane (see below).

Katz Dimer (XI, XII).[25] Norbornadiene dimerization to give a mixture of XI and XII (7:1 ratio) was accomplished with 5% Rh/C catalyst according to the procedure of Mrowca and Katz.[26] Yields ranged from 0-49% and were dependent on the batch of catalyst used and other unknown variables.

Hydrogenation of Pentacyclo[8.1.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (Norbornadiene Dimer) (X)[15]. Commercial norbornadiene dimer mixture (Aldrich) (104.0 g) (consisting of 26% Xa, 71% Xb, 3% Xc) (Table II) was partially dissolved in 106 g of absolute ethanol. To this 0.3 g of PtO_2 catalyst was added and the mixture was hydrogenated on a Parr apparatus at 3 atm hydrogen pressure at room temperature for 1.5 hours. The solution was diluted with water and extracted with pentane. The combined organic layers were dried over $MgSO_4$ and evaporated to give 98.0 g of an oil which solidified upon standing; glc analysis on a 10% Carbowax 20 M column (3 m x 6 mm, 200°) indicated a mixture consisting of 26% VIa, 71% VIb and 3% VIc. The compounds were not further purified or separated. Arnold, Trecker and Whipple[15] describe the preparation of VIa and VIb by hydrogenation from Xa and Xb. Both are low melting solids. Nmr of our hydrogenated mixture indicated loss of vinyl protons.

Partial Hydrogenation of Katz Dimer (XI, XII) in Ethanol. A solution containing 100 ml absolute ethanol, 16.8 g (0.082 mole) XI, XII (bp 76-77°/0.8 mm) and 0.05 g PtO_2 catalyst was shaken in a Parr apparatus at room temperature under 2.8 atm hydrogen pressure. After 1 hour, the uptake of hydrogen ceased and the mixture was worked up as above. Removal of solvent left 16.5 g of oil which was distilled, bp 150°/5 mm; glc (10% Apiezon-L, 3 m x 3 mm, 200°), indicated 1 major peak with the same retention time (8.1 min) as starting material XI, XII; mass spectrum m/e (rel intensity) 186 (M^+) (100), 171, 158, 157, 143, 132, 131, 130, 129, 121, 120, 119, 118, 117, 106, 105, 98, 95, 93, 92, 91, 83, 79, 66, 65, 64; nmr ($CDCl_3$) showed the absence of vinyl protons in δ 4.0-6.0 region, but the presence of cyclopropyl protons at δ 0.75 (d); other resonances were at δ 0.91 (s), 1.09 (m), 1.32 (s-br), 1.88 (d J ≅ 2Hz), 2.33 (br).

Hydrogenation of Katz Dimer (XI, XII) in Acetic Acid. Katz dimer (XI, XII) (5.0 g) in 150 ml of glacial acetic acid with 0.5 g PtO_2 catalyst was shaken in a Parr hydrogenator under 3 atm hydrogen pressure at room temperature until the uptake of hydrogen ceased (about 3 hours). The catalyst was removed by filtration and the mixture diluted with 100 ml of water and extracted with 3 x 100 ml methylene chloride. The organic layers were collected and dried over $MgSO_4$. Removal of solvent left 4.9 g of oil which was distilled at 83-88°/1.2 mm; glc (15% Apiezon L, 6 m x 3 mm column, 200°) revealed two peaks with retention times of 19.5 min (15%) and 23.5 min (85%) corresponding to compounds XVIIb and XVIIa. The mixture was not further separated; mass spectrum m/e (rel intensity) 188 (M^+) (100), 186, 181, 160, 159, 148, 147, 145, 134, 131, 122, 121, 120, 119, 118, 117, 107, 106, 105, 95, 94, 93, 92, 91, 79, 78, 77, 67; nmr ($CDCl_3$) shows absence of vinyl and cyclopropyl protons and gives only complex splitting between δ 0.7-2.45. This material has also been prepared by McKervey[13] similarly.

Reaction of Dihydro Katz Dimer (XVI) With Sulfuric Acid and Methylcyclohexane. To 200 ml of 97% sulfuric acid was added dropwise with cooling 8.0 g of XVI dissolved in 100 ml of methylcyclohexane. After stirring overnight at room temperature, the layers were separated. The methylcyclohexane layer was washed with 100 ml H_2O and dried over $MgSO_4$. Removal of solvent left 7.36 g of oil (91% yield) which was distilled and three fractions collected all boiling at 1 mm in the range 80-85°. Low melting solid separated in the last two fractions. The glc spectra on a 15% Apiezon L (6 m x 3 mm column, 200°) of fractions were virtually identical and showed 2 peaks with retention times

20.8 min (85%) and 22.1 min (15%); mass spectrum m/e (rel intensity) 188 (M^+) (100), 179, 173, 160, 159, 147, 146, 145, 134, 131, 109, 105, 97, 95, 93, 92, 91; nmr ($CDCl_3$) shows absence of cyclopropyl protons, δ 0.86 (d, br), 1.13 (br), 1.36 (d, br), 1.87 (d), 2.0 (m), 2.47 (br); ^{13}C-nmr (CCl_4, ppm from TMS) 57.5 $(CH)_2$, 48.0 (CH), 44.8 (CH) + (CH_2) or $(CH)_2$, 41.6 $(CH)_3$ + (CH_2) or $(CH)_2$ + $(CH_2)_2$, 40.1 (CH_2), 34.4 (CH) + (CH_2), 29.1 $(CH_2)_2$.[34] Nine different carbon atoms are indicated with two degeneracies and are consistent with cleavage of one of the two equivalent cyclopropane bonds to give XVIII.

Bromination of 4-Methylcyclohexene.[52] 4-Methylcyclohexene (Aldrich, 48 g, 0.5 mole) and N-bromosuccinimide (Aldrich, 18.3 g, 0.1 mole) in 75 ml of carbon tetrachloride were heated to reflux under magnetic stirring for 20 minutes. After keeping the mixture in a refrigerator overnight, precipitated succinimide was collected (9.7 g, 93%). The filtrate was evaporated to give a dark colored oil, which upon distillation gave 12.6 g of pale yellow green liquid, bp 55-58°/10 mm; glc, (DC 710, copper column 6 m x 6 mm, 210°), indicated two main components; mass spectrum m/e 176, 174, 96, 79; nmr (CCl_4) δ 5.64 (d, J ≅ 2Hz, 2H), 4.65 (m, 1H, CHBr), 2.5-1.25 (complex, 6H), 1.2-0.9 (complex 3H, CH_3). The mixture was not further characterized.

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(52) S.W. Staley, Ph.D. Thesis, Yale University, 1964.

1- and 6-Methyl-1,3-cyclohexadiene (XIXa) (XIXb). A mixture of 330 g (ca. 1.83 moles) of the above brominated 4-methylcyclohexene and 500 g (4 moles) of quinoline was heated at 130-180° under a stream of nitrogen. The distillate was collected in a receiver cooled by ice, washed with dil HCl and water,

dried over $CaCl_2$ and distilled to give 87.6 g (70%) of colorless hydrocarbon, bp 99-105°; mass spectrum m/e (rel intensity) 110 (M^+) (100) 94, 92, 91; 79 and 77; nmr (CCl_4) δ 6.0-5.3 (4.5 H), 2.9-1.6 (3.5 H), 1.03 (d, J ≅ 7 H, 2.9 H); the product appears to be a mixture of XIXa and XIXb.

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.50; H, 10.40.

Preparation of XX. The Diels Alder reaction was carried out under similar conditions as reported by Soloway[53] for the preparation of the parent hydrocarbon of XXXVII. A mixture of 87.6 g (0.40 mole) of XIXa/XIXb and 497 g (5.30 mole) of norbornene was heated with a small amount of hydroquinone in a glass pressure bottle at 170-180° for 24 hours. Distillation of the reaction mixture gave 29.7 g of milky, high boiling product, bp 64-66°/1 mm; glc, two components of equal intensity, possibly XXa and XXb; mass spectrum, m/e (rel intensity) 188 (M^+) (10), 173 (2), 146 (26), 94, 79 (37), 77 (11); nmr (CCl_4) δ 6.2-5.4 (complex, olefinic, 2H), 2.6-0.4 (complex, aliphatic, 19 H), 1.12 (s, methyl at bridgehead), 0.69 (d, J ≅ 7 Hz, methyl at non-bridgehead).

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(53) S.B. Soloway, J. Amer. Chem. Soc., 74, 1027 (1952).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.25; H, 10.90.

Preparation of XXIa/XXIb. Under conditions similar to those used by Scharf[54] for the preparation of the parent hydrocarbon of XXIV, precursor XX (28.92 g) in 1.22 liters of acetone (ACS grade) was irradiated with a 450 W. Hanovia medium pressure mercury lamp with a pyrex filter under nitrogen and with magnetic stirring for 209 hours at room temperature. Evaporation of

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(54) H.D. Scharf, Tetrahedron, 23, 3057 (1967).

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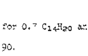
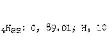
solvent left 13.1 g of liquid which upon distillation gave 8.8 g of an oil, bp 75-80°/1 mm; glc indicated at least eight peaks, of which the three major ones were XX (18%), XXIa-XXIb (38%), and XXXVII (40%). The mass spectrum of the mixture (m/e 190 (M^+) (40)), indicates that reduction had taken place to a large extent during irradiation, consistent with the assignment of structure XXXVII.



XXXVIIa



XXXVIIb

Anal. Calcd for 0.7 $C_{14}H_{20}$ and 0.3 $C_{14}H_{22}$: C, 89.01; H, 10.89. Found: C, 89.09; H, 10.90.

Ethylcyclopentadiene (XXII). Prepared according to the procedure of Alder and Ache[55] from sodium cyclopentadienide and ethyl bromide in liquid ammonia.

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(55) K. Alder and H.J. Ache, Ber., 95, 503 (1962).

Ethyl-exo-endo tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-10-ene (XXIII).[53] Essentially the same conditions as for the preparation of XX were employed. Freshly distilled norbornene (bp 95°, 300 g) was heated with 151 g of ethylcyclopentadiene in a glass pressure bottle in the presence of a trace of hydroquinone at 191-3° for 15 hours. Distillation of the reaction mixture gave 223.8 g of a clear liquid (bp 99-108°/4 mm); glc indicated higher boiling impurities, but not the dimer of ethyl cyclopentadiene; nmr δ 0.54

(d, J ≅ 10 Hz, inner proton of methylene bridge),[56] 2.60 (d, J ≅ 10 Hz, outer protons of methylene bridge).

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Preparation of XXIV.[54] Tetracyclic hydrocarbon mixture XXIII (204 g) in 5 liters of acetone was irradiated under the same conditions as XX for 113 hours. Direct distillation of the photolyzed mixture gave 176 g of colorless product, bp 65-87°/1 mm. The pot residue contained 44.1 g of viscous oil, which could be the acetone adduct.[54] The mass spectrum of the distilled product indicated 40% reduction of $C_{14}H_{20}$ to $C_{14}H_{22}$ (m/e 188: 190: 53-39); the nmr indicated the presence of olefinic protons. The process must sometimes be repeated to complete the reaction.

Sludge Catalyst.[20, 18-23] To a solution of 20 g (0.075 mole) of $AlBr_3$ in 50 ml of cyclohexane in a flask fitted with a reflux condenser, dropping funnel and drying tube was added dropwise 7 g (0.05 mole) of t-butyl bromide, diluted with an equal volume of cyclohexane. The reaction was left stirring overnight at room temperature. However, the reaction may be accelerated by slight warming of the reaction vessel. The reaction is usually over after evolution of HBr ceases and the clear yellow catalyst (about 20 g) separates. This catalyst may be kept for prolonged periods under cyclohexane in a vessel stopped with a drying tube and may be reactivated, if necessary, by addition of small amounts of $AlBr_3$.

Preparation of Diamantane. From Tetrahydro-Binor-S (XXVII/XXVIII) With Aluminum Bromide. Tetrahydro-Binor-S (XXVII/XXVIII) (100 g, 0.54 mole)

was added from a dropping funnel to a cyclohexane solution (100 ml) containing 27 g aluminum bromide. After the exothermic reaction subsided, the reaction was refluxed gently for an additional two to three hours. The cyclohexane layer was decanted carefully. The catalyst was washed several times with hot cyclohexane. The combined extracts were then washed with water and dried over $MgSO_4$. Evaporation of solvent left a semisolid residue which was partially dissolved in about 100 ml of pentane. The white solid was filtered and the solution was further concentrated until diamantane no longer precipitated. The total amount of diamantane obtained upon drying was 62-75 g (62-75%), mp 240-241° ; glc (10% Carbowax 20 M, 3 m x 3 mm column 180°) of precipitated material indicated only one peak; the mother liquor contained mostly disproportionation product VII; relative retention times are 8.4 and 11 min for VII and I, respectively; nmr ($CDCl_3$) of I showed a single peak δ 1.68. The diamantane so obtained may be used without further purification for further conversions. Recrystallization from pentane gives white crystals, mp 244.0-245.0° (lit.[13] mp 251° after purification by zone refining).

From Tetrahydro-Binor-S (XXVII/XXVIII) with Sludge Catalyst. To 20 ml of sludge catalyst was added dropwise 1.0 g of XXVII/XXVIII dissolved in 5 ml of cyclohexane. Heat was evolved. After refluxing for five hours, [illegible] of the starting material had reacted. The product was diluted with 15 ml cyclohexane and decanted. The catalyst was washed several times with hot cyclohexane. The combined organic layers (250 ml) were washed twice with water (100 ml), dried over $MgSO_4$, and the solvent evaporated. To the semisolid residue, consisting of 90% diamantane, 7% VII, and 3% other unidentified products, acetone was added; upon cooling the white crystals which formed were collected. Total yield of diamantane was 0.71 g (71%).

General Isomerization Procedure For Starting Materials VI, VIa, XIII XVI, XVII, XVIII, XXI, XXIV, XXXV. Each precursor was dissolved in carbon disulfide or cyclohexane in a flask equipped with a condenser and stirrer. The catalyst was then added slowly. The flask was cooled to moderate the initial exothermic process. The reaction was allowed to warm to room temperature and was then heated at the temperatures and for the periods of time indicated in Table VI. Workup involved decanting the organic layer and extracting the catalyst layer with either carbon disulfide or hot cyclohexane. The decanted layer and extracts were combined, washed with water, dried over $MgSO_4$ and evaporated. If an oil was obtained, this was generally taken up in a small amount of pentane and diamantane was crystallized from a dry ice-acetone bath. Sometimes a rapid filtration through alumina was necessary before any crystals of diamantane were obtained.

From Binor-S (XIII) With Sulfuric Acid. Binor-S (2.0 g) was added slowly with stirring to 10 ml of 97% sulfuric acid. After the initial exothermic reaction had subsided, the reaction mixture (which had turned dark red) was stirred for 48 hours. The mixture was poured into ice water, separated, and the aqueous layer extracted with ethyl ether. The combined ether extracts were washed with water and dried over $MgSO_4$. The solvent was then evaporated under reduced pressure to give an oily residue consisting of diamantane (I), diamantanone, and other products. This residue was dissolved in petroleum ether and chromatographed on alumina. Diamantane was the first to elute with pentane (0.6 g, 30% yield). After all the diamantane had eluted, the solvent was changed to benzene (a small amount of unidentified material was obtained), and finally to ethyl ether. The ether fraction contained 0.3 g of material (15% yield), which had identical ir and nmr spectra with those of diamantanone. Characterization and identification of other products were not pursued.

TABLE VI

SUMMARY OF DIAMANTANE PREPARATIONS FROM VARIOUS PRECURSORS

Starting Material	g	Solvent (ml)	Catalyst[b]	Temp	Time, hrs	Products	
						Diamantane (Isolated)	Other
XXVII/XXVIII	1.0	C_6H_{12} (5)	Sludge (2.0 ml)	Reflux	5	0.71 g (71%)	VII (6-7%)
XXVII/XXVIII	100.0	C_6H_{12} (100)	$AlBr_3$ (27 g)	Reflux	2-3	62-75 g (62-75%)	VII (6-7%)
XXXV	0.5	C_6H_{12} (5)	$AlBr_3$ (0.25 g)	Reflux	2-3	0.42 g (84%)	VII (0.32 g, 6.4%)
XXXVI + XXXV + I + XII[c]	1.82	C_6H_{12} (10)	$AlBr_3$ (0.5 g)	Reflux	2-3	1.27 g (70%)	VII (6-7%)
XIII	11.0	C_6H_{12} (25)	Sludge (2 ml)	Reflux	4-5	5.5 g (10%)	VII
XIII	2.0	none	97% H_2SO_4 (10 ml)	25°	48	0.6 g (30%)	Diamantanone (0.3 g, 15%)
XVII	1.0	C_6H_{12} (5)	$AlBr_3$ (1.0 g)	Reflux	24	0.25 g (25%)	VII
XVII	1.0	C_6H_{12} (5)	Sludge (2 ml)	Reflux	24	0.20 g (20%)	VII
XVIII	1.0	C_6H_{12} (5)	$AlBr_3$ (2 ml)	Reflux	24	0.25 g (25%)	VII
XVIII	1.0	C_6H_{12} (5)	Sludge (2 ml)	Reflux	24	0.18 g (18%)	VII

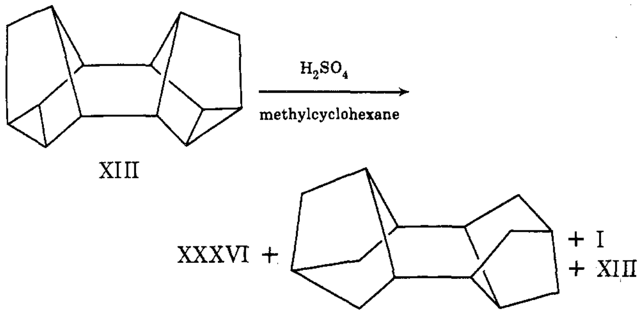
TABLE VI cont.

Starting Material	g	Solvent (ml)	Catalyst[b]	Temp	Time, hrs	Products	
						Diamantane (Isolated)	Other
XVI	18.5	CS_2 (25)	Sludge (20 ml)	70-100°	4-24	10-16%	VII and alkyl adamantanes
XVI	18.5	none	Sludge (20 ml)	70-100°	4-24	~16%	VII and alkyl adamantanes
VIa[d]	10.0	none	Sludge (7 ml)	65°	72	1.0 g (10%)	VII
VI[e]	10.0	CS_2 (20)	Sludge (10 ml)	100°	19	< 5%	VII (4.0 g, 40%)
VI[f]	10.0	CS_2 (20)	Sludge (10 ml)	80°	48	1-5%	VII (4.0 g, 40%)
XXI	1.66	none	Sludge (3 ml)	85°	6-10	47% by glc	(XXVI)
XXI	0.5	CS_2 (20)	Sludge (0.5 ml)	90-100°	6-10	41% by glc	(XXV)
XXIV	125.3	none	Sludge (215 ml)	89-95°	4.5	31.6 g (25%)	36.0 g (29%) alkyl adamantanes

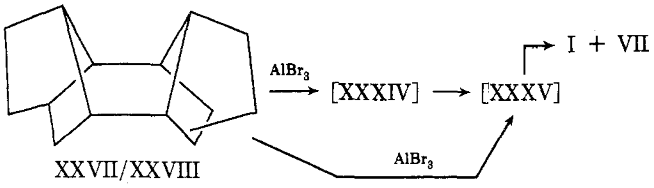
[a] In all instances besides VII, other fragmentation products were obtained which ranged from small to large amounts. [b] "Sludge" refers to catalyst prepared from t-butyl bromide-aluminum bromide, (see experimental). [c] Mixture from reaction of XIII with H_2SO_4-methylcyclohexane consisting of XXXVI (56.5%), XXXV (37.6%), I (15%) and XII (5%). [d] From Cu_2Cl_2 sensitized photolysis of norbornene, cf. refs 15 and 16. [e] From hydrogenation of commercial (Aldrich) 2+2 norbornadiene dimer mixture; the hydrogenated material consists of 26% VIa, 71% VIb, and 3% VIc. [f] From acetone sensitized photodimerization of norbornene consisting of 12% VIa, and 88% VIb, cf. refs 15 and 16.

graphical representation of product composition *vs.* time, illustrates the course of a typical rearrangement.

We have also isolated XXXV by hydride transfer reduction of Binor-S (XIII) by the sulfuric acid–methylcyclohexane method[31] at 0°. After 0.5 hr under the conditions used, two major components, XXXVI (34%) (which has not been identified) and XXXV (51%), as well as diamantane (5%) and unreacted Binor-S (6%), were observed by gas chromatographic analysis. XXXV was isolated by crystallization and shown to be identical with the second intermediate observed in the aluminum bromide isomerization. The ^{13}C nmr spectrum[34] of XXXV consisted of five lines. Although XXIX also has five unique carbons, XXXV is more compatible with the chemical shift data[34] and is less strained [$\Delta H_f°$ (calcd) = −13.21 kcal/mol, strain (calcd) = 34.85 kcal/mol].[17] *trans*-Pentacyclo[8.2.1.1.^{2,5}.0^{3,7}.0^{8,12}]tetradecane (XXXV) isomerizes without intervention of other glc-detectable intermediates to diamantane (I) and VII in 84 and 6.4% yields, respectively.



XXXV



XXVII/XXVIII

The mechanism of the rearrangement of XXVIII to I has been analyzed exhaustively by graph theoretical techniques involving generation and energetic evaluation of possible routes. A complete account of this treatment will be published separately.[1e]

The diamantane obtained from precursor XXVII or XXVIII is quite pure. Yields of diamantane were as high as 75%, and average overall yields from Binor-S are about 65–70%.[12] McKervey[13] has verified our results independently and has used dichloromethane as solvent with even higher yields, although some chlorinated by-product is formed as a result. Diamantane is now readily available in greater than 50% overall yield in three steps from norbornadiene, and is almost as easy to obtain as adamantane.

Conclusion

Diamantane (I) is readily prepared from Lewis acid catalyzed rearrangement of hydrogenated Binor-S (XXVII/XXVIII) in ~70% yield, and in three steps from commercial norbornadiene in an overall yield of >50%. Other $C_{14}H_{20}$ pentacyclic precursors give lower yields, with the exception of *trans*-tetrahydro-Binor-S (XXXV); however, the preparation of pure XXXV is more cumbersome. In all cases, in addition to diamantane (I), there was isolated a disproportionation product (VII), and the proportions of I to VII varied with the type of precursor. Other catalysts such as the aluminum bromide–*tert*-butyl bromide "sludge" catalyst did not markedly affect the yield, nor did varying the solvent. The large variation of yield with starting material may be explained by mechanistic considerations, as is discussed in a separate paper.[1e]

The structural and spectral properties of I are summarized and are in agreement with expectations for a diamond lattice hydrocarbon.

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Registry No.—I, 2292-79-7; X, 5307-65-3; XI, 17926-99-7; XII, 17926-98-6; XIXa, 1489-56-1; XIXb, 19656-98-5; XXa, 51966-20-2; XXb, 52032-36-7; XXIII, 51982-56-0; XXXVIIa, 52032-37-8; XXXVIIb, 52032-38-9; 4-methylcyclohexene, 591-47-9.

Miniprint Material Available. Full-sized photocopies of the miniprinted material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the miniprinted and supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2979.

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Diamantane. II.[1] Preparation of Derivatives of Diamantane

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Methods have been developed for the conversion of diamantane (I) to the three possible types of monofunctional derivatives: 1- (medial), 3- (secondary), and 4- (apical). The 1-diamantyl cation is the most stable and most readily generated by hydride abstraction. Kinetically controlled nucleophilic attack on this cation can be made to give 1-bromodiamantane (III) and 1-diamantanecarboxylic acid (V) in liquid bromine and under Koch–Haaf conditions, respectively. Sulfuric acid oxidation of I affords 3-diamantanone (X), a convenient source of other 3-diamantyl derivatives. The secondary 3-diamantyl tosylate (XII) solvolyzes about 3.5 times faster than 2-adamantyl tosylate. Under equilibrium conditions apical adamantyl derivatives are favored by enthalpy over their medial isomers, but the entropy effect is opposite. The enthalpy term for relatively large groups such as methyl dominates. Thus, 4-methyldiamantane (XXIII) can be synthesized by isomerization of the other methyldiamantanes or of other pentacyclotetradecanes, such as XXII, XXV, or XXVI. The equilibrium is less one-sided for smaller substituents, *e.g.*, halide and alcohols, and preparations of apical products require chromatographic separation since they are seriously contaminated by their medial isomers. ^{1}H nmr chemical shifts of the various types of diamantane derivatives can be predicted satisfactorily by using additivity increments obtained from similarly constituted adamantanes.

The preparation of functional derivatives of diamantane (I) depended on the availability of the parent hydrocarbon.[1a] When the yield of I was improved to 10% by employing the exo-trans-exo norbornene dimer as precursor and aluminum bromide sludge catalyst,[3] the study of the chemistry of diamantane began.[3–5] The reactions employed were modeled after those which had been used successfully on the first member of the diamondoid series, adamantane (II).[6]

Bromination of diamantane by neat bromine led to bridgehead substitution, but, unlike adamantane, two isomers, medial[7] (1-) and apical[7] (4-), were possible. Nmr