Thermal and Photochemical Interconversion of Several 1,8-Naphtho(C_4H_4) Hydrocarbons. Tests of the Woodward–Hoffmann Rules

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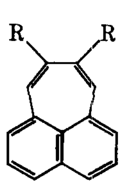
Received July 7, 1976

The photochemical and thermal interconversions of both deuterated and nondeuterated pleiadiene (1), 1,8-naphthobicyclo[3.2.0]hepta-2,6-diene (2), and 1,8-naphthotricyclo[4.1.0.0^{2,7}]heptene (3) are reported. All of these isomerizations may be preliminarily explained in terms of allowed and forbidden pathways. For several of the reported examples, however, a more complex interpretation is required by the experimental data.

Even though there has been much work done on the higher members of the pleiadiene family,[2] there are only a few reports on the preparation and isomerizations of the parent molecule (**1a**) and the isomeric molecules **2a** and **3a.**[3] Literature records the formation of pleiadiene (**1a**) from 1,8-naphthobicyclo[3.2.0]hepta-2,6-diene (**2a**) by an unusual two-photon process,[3a] and also by thermal isomerization at high temperatures (250 °C), a process which is forbidden in the Woodward–Hoffmann sense.[3a,b] On the other hand, **1a** could be obtained by the photolysis of 1,8-naphthotricyclo[4.1.0.0^{2,7}]heptene (**3a**), whereas heating **3a** resulted in the exclusive formation of **2a.**[3b] Our work described here was an attempt to trace the origin and paths for these isomerizations.



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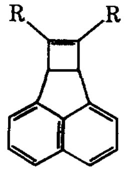

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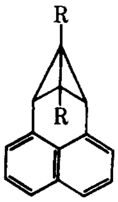
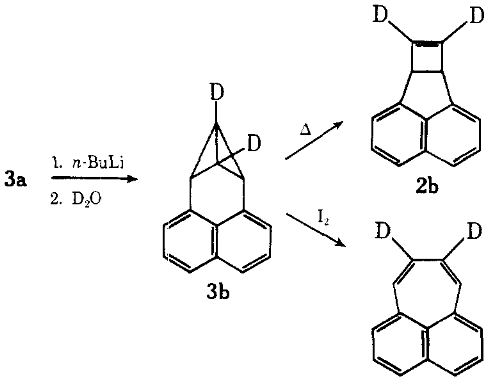


3

a, R = H; **b**, R = D

Preparation of Hydrocarbons. The preparation and purification of the nondeuterated hydrocarbons **1a, 2a,** and **3a** has been described previously.[4] Compound **3b** was prepared by treating an ether solution of **3a** with excess n-butyllithium followed by quenching with D_2O. Thermal isomerization of **3b** then afforded **2b,** while treatment of **3b** with a catalytic amount of I_2 afforded pleiadiene-d_2 (**1b**).[5]

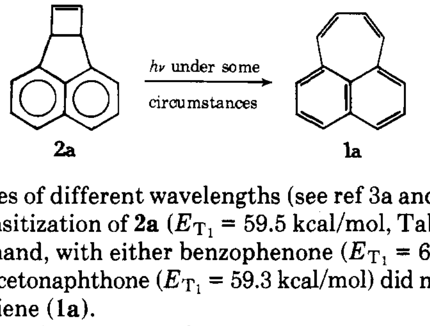


(1)

(2)

Absorption and Emission Studies. The absorption and emission parameters of both **2a** and **3a** closely resemble those of naphthalene, whereas those of **1a** are markedly different. The absorption of **1a** extends up to 570 nm, which makes the compound red.[2a] The fluorescence of **2a** and **3a** resembled the fluorescence of naphthalene, was structured, and extended from 325 to 390 nm at room temperature in ether, cyclohexane, acetonitrile, and EPA. Both **2a** and **3a** had a long-lived phosphorescence ($\tau \sim 3$ s) in the region 480–600 nm at 77 K in EPA glass; however, no phosphorescence from **2a** or **3a** was observed in solution at room temperature. Unfortunately, pleiadiene (**1a**) did not show any emission either at low or room temperature. The spectroscopic data are summarized in Table I.

Photoisomerization of 2a into 1a. As has been reported by Meinwald and co-workers,[3a] **2a** was found to be totally inert upon direct irradiation ($\Phi < 10^{-4}$) at room temperature in a variety of solvents. This is particularly intriguing because the photoisomerization of **2a** into **1a** did occur upon direct irradiation at 77 K (450-W medium-pressure lamp) in 3-methylpentane (3-MP). Furthermore, the photoreaction will occur at low temperature if **2a** is irradiated simultaneously with two light sources of different wavelengths (see ref 3a and below). Triplet sensitization of **2a** (E_{T_1} = 59.5 kcal/mol, Table I), on the other hand, with either benzophenone (E_{T_1} = 69.5 kcal/mol) or 2-acetonaphthone (E_{T_1} = 59.3 kcal/mol) did not afford any pleiadiene (**1a**).



(3)

The above data suggest that the lowest singlet (S_1) and triplet states of **2a** are not responsible for the isomerization. By what mechanism is **2a** converted into pleiadiene (**1a**)? The following observations strongly suggest that the photoisomerization occurs from an upper triplet state of **2a.**

First, keep in mnd that 1,8-naphthobicyclo[3.2.0]hepta-2,6-diene (**2a**) has no electronic absorption above 330 nm. Irradiation of **2a** at 77 K in 3-MP or EPA with monochromatic light at 260 ± 10 nm (**2a** has $\epsilon \sim 2 \times 10^3$ in this region) did not give **1a.** This establishes that the lowest singlet state (S_1) of **2a** is insufficient to bring about the reaction. But the product was obtained at 77 K in less than 1 h when the irradiation was conducted with two lamps, one exciting **2a** at S_1 (λ 260 ± 10 nm) and the other above 350 nm (450-W xenon–mercury lamp with Corning glass filter 3-75), at right angles. Irradiation of **2a** with the above two light sources at room temperature, however, did not yield any **1a.** These results suggest that a second photon absorption must occur before the reaction can take place and that the species absorbing the second photon is long lived at 77 K but not at room temperature. Because T_1 of **2a** has a lifetime of 3.3 s at 77 K, while S_1 has a lifetime of only 48×10^{-9} s at 77 K ($\tau = 33 \times 10^{-9}$ s at 295 K), T_1 seems a likely candidate for the species absorbing the second photon.

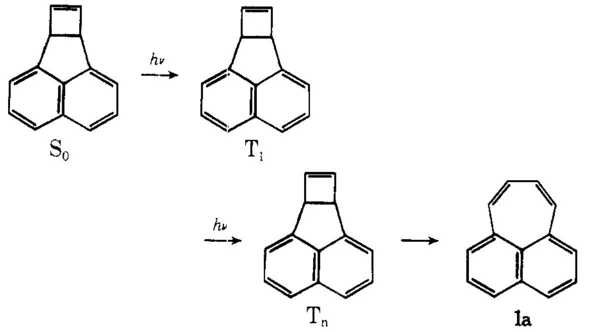
An interesting result was obtained when the wavelength of

Table I. Spectroscopic Properties of 1a, 2a, and 3a

	E_{S_1},[a] kcal/mol	E_{T_1},[b] kcal/mol	τ_{S_1}, s (77 K)[c]	τ_{S_1}, s (275 K)[d]	τ_{T_1},[e] s (77 K)	Φ_{fl}
Naphthalene	91	61		96×10^{-9}	2.4	0.10
1a	51	?	No emission from S^1 or T^1 at room temperature or 77 K			
2a	88	59.5	48×10^{-9}	33×10^{-9}	3.3	0.40[f]
3a	88	59.5	43×10^{-9}	36×10^{-9}	2.8	0.47[f]

[a] Values are based on the fluorescence spectrum; in the case of 1a it was based on the absorption spectrum. [b] Values are based on phosphorescence emission. [c] The lifetimes were measured by the single photon counting technique in EPA glass. [d] The lifetimes were measured in CH_3CN (1×10^{-3} M) under N_2. [e] The triplet lifetime was measured by flash photolysis in EPA glass. [f] The quantum yields are based on the value of 0.60 for acenaphthene and maintaining the OD at 296 nm as 0.2.

the secondary light source was changed. No product was formed when the secondary source had λ <350 nm or >440 nm; irradiation in the region of 350–440 nm, however, did produce pleiadiene (**1a**). Since naphthalene triplets undergo T–T transitions in the 350–440-nm region[6] and the absorption and emission properties of **2a** are so similar to those of naphthalene, **2a** would be expected to also have T–T transitions in the same region. The rough correspondence of product formation and T–T absorption leads us to believe that the reaction originates from a higher triplet (eq 4) as suggest earlier for related compounds.[2]



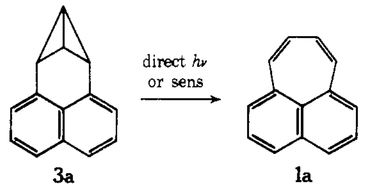
(4)

The results above have clearly demonstrated the existence of an energy barrier in going from **2a** to **1a** from both S_1 and T_1. The absence of formation of **1a** upon irradiation, either direct or triplet sensitization, up to 90 °C is consistent with the postulate that vibrationally excited T_1 is not the reactive species.

One other point should be mentioned about the photoisomerization, **2a** → **1a**. The reaction occuring from T_n of **2a** could in fact generate **1a** in the excited state by an adiabatic photoprocess. Both singlet (S_1) and triplet (T_1) energies of **2a** are well above those of **1a**.[7] Unfortunately, the detection of an excited state of **1a** was not possible for several reasons. Firstly, pleiadiene does not emit light from its S_1 and T_1 states. Secondly, the triplet state (T_1) of pleiadiene (**1a**), the likely excited state product of the reaction, is so low in energy[7] that efficient energy transfer to another molecule which does emit is precluded. Finally, photolysis of pleiadiene does notgive a "unique" product (see below) whose appearance in the photolysis of **2a** would indicate that pleiadiene is formed in the excited state.

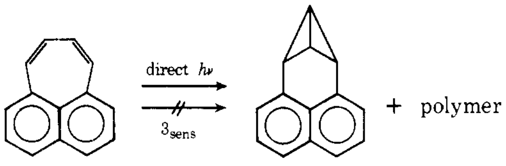
The disrotatory opening of cyclobutenes to butadienes is normally an allowed process in the excited state. Both the S_1 and T_1 state of cyclobutenes have been shown to correlate with the corresponding excited states of butadienes by theoretical calculations.[8] Intuitively, one would expect the S_1 and T_1 states of the cyclobutene (**2a**) also to correlate with the corresponding states of the butadiene (**1a**). The actual diagram, as originally constructed by Michl,[9] would indicate otherwise. The lowest excited state of **2a**, for example, correlates with an unusual doubly excited state of **1a**. Likewise, there is no correlation between the lowest excited state of **1a** and its counterpart in **2a**. Michl has concluded that for systems having this unusual type of correlation diagram there should be large barriers to reaction in the excited state.[2,9] The photoisomerization of **2a** → **1a** represents another example where this predicted phenomenon has actually been observed.

Photointerconversion of 3a and 1a. Unlike the unusual behavior of **2a** upon excitation, **3a** was smoothly converted into **1a** from either the S_1 or T_1 state. Direct irradiation of **3a** (<300 nm) in various solvents gave pleiadiene (**1a**) as determined by NMR, uv, and VPC retention time. Sensitization of **3a** with either benzophenone or 2-acetonaphthone also affords **1a**.



3a 1a (5)

Irradiation of pleiadiene (**1a**) either at S_1 (<460 nm) or S_2 (>280 nm) gave a product mixture which was mainly a polymeric material plus less than 15% of **3a** which was identified by uv, VPC retention time, and mass spectrometry. Triplet sensitization of **1a** with benzophenone and 2-acetonaphthone, both of which should have triplet excitation energies greatly in excess of that anticipated for pleiadiene (**1a**),[7] failed to produce either **2a** or **3a**.



1a 3a (6)

Although **1a** and **3a** interconvert photochemically, it is clear that the interconversion pathways differ in some fundamental way. It would seem reasonable that **3a** isomerizes to **1a** in its S_1 and T_1 states by a symmetry-allowed ring opening. That the frontier orbital of **3a**, the lowest antibonding orbital of **3a**, may have a dominant role in determining the course of the reaction is borne out by the fact that the radical anion of the bicyclobutane (**3a**), whose highest occupied molecular orbital (MO) is identical with the highest occupied MO of S_1 and T_1 states of **3a**, ring opens to the radical anion of **1a**.[10]

$$3a^{\cdot -} \rightarrow 1a^{\cdot -} \quad (7)$$

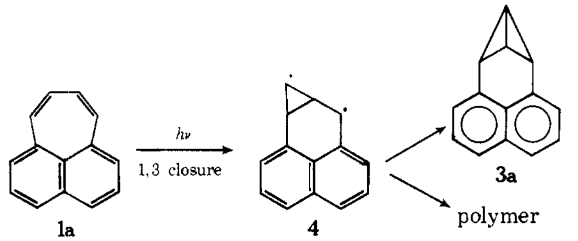
The reverse photoreaction must proceed differently because of the preponderant formation of polymer. Perusal of Table I shows that the lowest singlet and triplet excited states of **1a** arebelow any excited state of **3a**. This means that adiabatic photoconversion of **1a** into any excited state of **3a** is very unlikely. Furthermore, simple energy considerations suggest that the S_1 state of **1a** is above the ground state of **3a**, while the T_1

Table II. Activation Parameters for Thermal Rearrangements

Reaction	E_a, kcal/mol	Log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
3a → 2a[a]	32.9 ± 3.5	13.2 ± 3.2	32.1 ± 3.5	−1.0 ± 3.5
2a → 1a[b]	39.3 ± 0.8	14.6 ± 0.2	38.4 ± 0.8	5.5 ± 0.9

[a] The kinetics were run by NMR on the disappearance of 3a. [b] The kinetics were run by visible–uv on the appearance of 1a.

state is not. If this energetic array is correct, it would mean that S_1 state of pleiadiene (**1a**) could still isomerize to **3a**, perhaps in a stepwise fashion, but the T_1 state could not. This interpretation is in line with the experimental observations. A plausible mechanism for this isomerization is shown below.

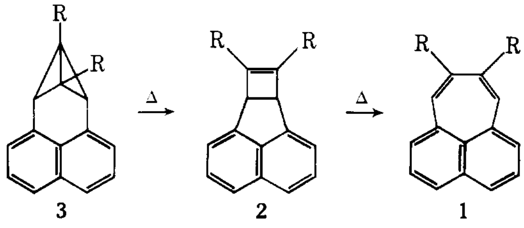


(8)

(9)

One other point concerning the photochemistry of **1a** is worth noting and that is the fact that **1a** does not isomerize to **2a**. This is perfectly understandable in light of Michl's correlation diagram discussed previously.[2]

Thermal Interconversion of Hydrocarbons. The thermal isomerizations of **1**, **2**, and **3**, both for the deuterated and nondeuterated hydrocarbons, are shown below.[3a,b,4] It would appear that at least in part the driving force for each of the reactions is relief of strain.



(10)

R = H and R = D

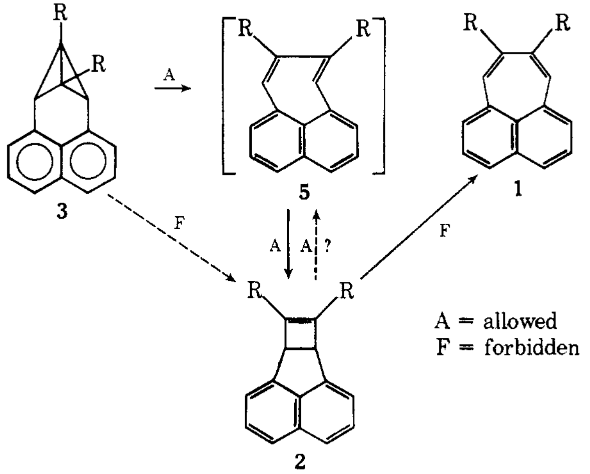
The activation parameters for each of the isomerizations were determined for the nondeuterated materials and are reported in Table II.

Both isomerizations could proceed either by symmetry-controlled pathways[3b] or by stepwise mechanisms involving the formation of biradical-like intermediates. The nature of the product in each reaction and the labeling experiments are perfectly consistent with the symmetry-controlled processes. However, as will be shown below, analysis of the activation parameters suggest that these reactions may proceed through biradical intermediates.

The conversion of the bicyclobutane (**3**) into the cyclobutene (**2**) can be explained by a two-step process involving an initial symmetry-allowed ring opening to give *cis,trans*-pleiadiene (**5**) followed by a symmetry-allowed conrotatory closure to give **2**. The cis,trans isomer (**5**), if formed, is not observed in the reaction for it would be a very strained molecule and it would be expected to isomerize very rapidly to **2** (Scheme I).

The conversion of **2** into pleiadiene (**1**) must of necessity involve a disrotatory ring opening of **2** which is a thermally forbidden reaction. This can be seen vividly in the previously described correlation diagram connecting **2** and **1**.[2,9] Conrotatory ring opening of **2**, which is thermally allowed, would form the very highly strained *cis,trans*-pleiadiene (**5**). It would appear in this case that if the conversion of **2** into **1** were a concerted reaction the allowed pathway would have a higher energy of activation than the forbidden one because of the anticipated strain energy associated with the allowed product (**5**). Even if the allowed process were to occur, the reaction would be hidden, for **5** should rapidly reclose to **2**.

Scheme I. Symmetry-Controlled Pathways for the Interconversion of 3 into 2 and 2 → 1



Are biradicals formed in the conversion of **3** into **2** or is this strictly a symmetry-controlled procss? A comparison of the activation parameters for this process with systems that undergo similar reactions (Table III) suggests that the initial reaction of **3** involves a single cleavage of a bicyclobutane bond. It can be seen that the energies of activation for the first three reactions in the table are much higher than the one reported in this work or the fourth entry. As a matter of fact, all the activation parameters are similar for the last two reactions described in Table III. Christl and co-workers have argued convincingly[11] that this fourth reaction proceeds via a biradical intermediate. The lower E_a for this process compared to the first three can be attributed to the stabilizing influence of the double bond in going from reactant to the biradical intermediate. In the naphthobicyclobutane (**3a**), stabilization by the naphthalene ring (benzylic stabilization) would have a comparable influence in lowering the E_a. This suggests that the thermal isomerization of **3** proceeds through initial formation of a biradical (Scheme II). Of course, without knowing how substituent effects alter the activation parameters one cannot be totally certain that this is the case.

Scheme II. Biradical Mechanism for the Thermal Isomerization of 3 into 2

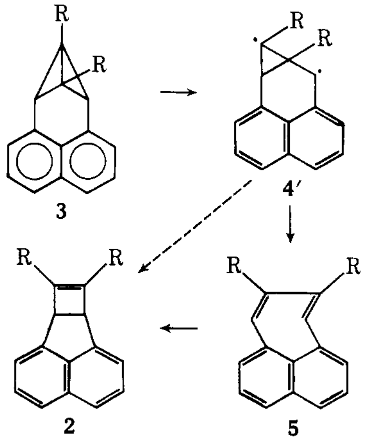
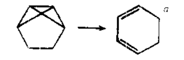
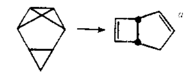
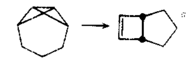
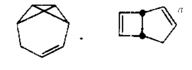
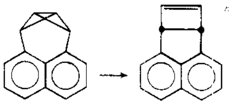
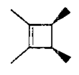
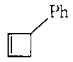
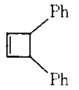
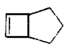
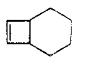
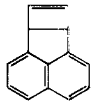


Table III. Comparison of Kinetics of Thermal Rearrangements of Endo,Endo' Bridged Bicyclobutanes

	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	E_a	Log A
 [a]	40.7 ± 1.0	0.6 ± 1.5	41.7 ± 1.0	13.6 ± 0.5
 [a]	37.6 ± 1.0	1.5 ± 1.0	38.5 ± 1.0	13.7 ± 0.5
 [a]	37.9 ± 1.5	−1.1 ± 3.0	38.8 ± 1.5	13.2 ± 0.7
 [a]	31.5 ± 0.6	1.1 ± 1.1	32.4 ± 0.6	13.6 ± 0.4
 [b]	32.1 ± 3.5	−1.0 ± 3.5	32.9 ± 3.5	13.2 ± 3.2

[a] Reference 11. [b] This work.

Table IV. Energies of Activation for Cyclobutene Ring Openings

Compd	E_a, kcal/mol	Ref
	32.70	*a*
	31.55	*b*
	37.30	15c
	26.00	*c*
	24.50	*d*
	45.86	15b
	43.20	15c
	39.30	This work

[a] W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, 80, 4220 (1958). [b] H. M. Frey, B. M. Pope, and R. F. Skinner, *Trans. Faraday Soc.*, 63, 1166 (1967). [c] M. Pomerantz and P. H. Hartman, *Tetrahedron Lett.*, 991 (1968). [d] J. I. Brauman and W. C. Archie, Jr., *Tetrahedron*, 27, 1275 (1971).

If the biradical 4′ [12] were formed, would it be expected to yield **2**? The answer is yes. Dewar has suggested convincingly[14] that the stereoselective ring opening of bicyclobutanes begin with a single bond cleavage. The resulting biradical "remembers" its origin and its subsequent selectivity is assumed. Similar reasoning can be applied to the present case.

Can we infer the existence of biradicals in the "forbidden" conversion of the cyclobutene (**2**) to pleiadiene (**1**) or is the process a truly concerted forbidden reaction? In other constrained cyclobutenes, where the energy of activation of the allowed conrotation is high, the isomerizations have been proposed to go through biradical intermediates to give nonstereospecific products.[15] A comparison of the activation energies for the ring opening of **2** with other cyclobutenes is shown in Table IV.

It can be seen that the activation energy for the ring opening of **2** is indeed higher than for those cases where an allowed conrotation is not prevented because of ring strain of the product. It would appear then that the "forbidden" character of the ring opening of **2** does influence the E_a for the reaction. On the other hand, the E_a's for the forbidden ring opening of bicyclo[3.2.0]heptene and bicyclo[4.2.0]octene are substantually higher than the value for **2**. The naphthalene π electrons must have a stabilizing influence on the ring opening as do phenyl groups of the simple cyclobutenes shown in the table. Whether one can attribute this lowering of the E_a to the formation of a stabilized benzylic biradical or some other effect cannot be known for certain at this time.

Another interesting aspect of the forbidden ring opening of **2** to pleiadiene (**1**) is that the reaction may be another example of a thermally induced chemiluminescent reaction. The activation energy (39.3 kcal/mol) coupled with the strain energy of the cyclobutene (29.8 kcal/mol) and the low values for E_{S_1} and E_{T_1} of the product (**1**) could produce **1** in either the S_1 or T_1 state. However, as mentioned previously, there are at present no practical methods for detecting the excited states of pleiadiene.

Concluding Remarks. The above data demonstrate that one must analyze very carefully those reactions for which the Woodward–Hoffmann rules can be applied, as with the thermal and photochemical isomerization of **2** into **1**. Other reactions which are fully in accord with the rules such as the thermal isomerization of **3** into **2** may actually proceed via biradicals. Much more experimental work will have to be done, however, to validate this interpretation.

Experimental Section

Emission spectra were recorded on a Perkin-Elmer Model MPF-3L spectrofluorimeter and electronic absorption spectra on Cary-17 instruments. NMR spectra were recorded on a Varian A-60 spectrometer. VPC analysis was made using a Varian Aerograph series 1200 equipped with flame ionization detector. The condition for the analysis of **1a**, **2a**, and **3a** was 5% 1,1-bis(2-cyanoethoxy)propane, 3 ft × 0.5 in. column at 110 °C. Under our VPC analysis condition partial conversion of **3a** to **1a** was observed. The singlet lifetime was measured using a home-built nanosecond singlet photon counter and triplet lifetime using a microsecond flash photolysis apparatus equipped with xenon lamp. Irradiations were conducted using a 450-W medium-pressure mercury lamp or 450- or 1000-W high-pressure xenon–mercury lamp using appropriate Corning glass filters or Aminco-Bowman monochromator.

Solvents used in the study (cyclohexane, ethyl ether, and acetonitrile) were once distilled before use. EPA (MCB phosphosimetry grade) and 3-MP (Aldrich 99+%) used for low-temperature study were passed once through an alumina column. Syntheses of compounds **1a**, **2a**, and **3a** are already in the literature.[4]

Kinetics of 3a to 2a. A solution of **3a** in cyclohexane was degassed and sealed in vacuo in an NMR tube. The tube was heated in a thermostated oil bath, and NMR measurements were made periodically after quenching the tube in water. The kinetics were followed by the disappearance of the bicyclobutane signals relative to an assumed constant aromatic region.

Kinetics of 2a to 1a. A solution of **2a** (6.7 × 10^{-3} M) in cyclohexane was placed in a visible–uv cell equipped with a graded seal and ground glass joint. The tube was sealed in vacuo. The cell was heated in a thermostated oil bath and measurements were made periodically after quenching the cell in the water. The kinetics were followed by the appearance of **1a** in the visible; an infinity reading was taken after heating the cell at >190 °C for 10 h.

Preparation of 3b. To a solution of 300 mg (1.69 mmol) of **3a** in 50 ml of ether under nitrogen was added 3.0 ml of 2.0 N *n*-butyllithium (6.0 mmol) in hexane. The resulting dark orange solution was stirred at room temperature for 1 h after which it was quenched with D_2O. Workup afforded an almost quantitative yield of **3b.** Mass spectral and NMR analysis revealed an 83% incorporation of deuterium into the bridgehead positions with less than 2% incorporation into the benzylic positions.

Preparation of 1b and 2b. These were prepared by the literature method used to prepare **1a** and **2a** only beginning with the **3b** described above.

Acknowledgment. The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589) and the National Science Foundation (Grants NSF-MPS70-02165 and NSF-MPS73-04672) for their generous support of this research and the authors also wish to thank Professor G. Schuster for assistance in the early phase of the work. The authors at the University of Tennessee wish to thank the Research Corporation for their generous support of this work.

Registry No.—**1a,** 208-20-8; **2a,** 30736-79-9; **3a,** 40480-63-5.

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Stepwise Elaboration of Diamondoid Hydrocarbons. Synthesis of Diamantane from Adamantane

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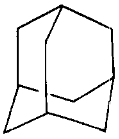
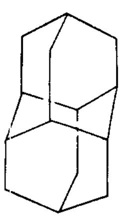
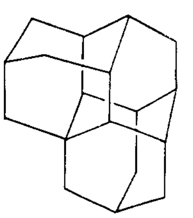
Received June 1, 1976

Diamantane (**2**) has been synthesized in a stepwise manner starting with adamantane (**1**). The key steps involve functionalization, ring closures by diazo ketone-derived carbene insertions (**7** → **8** and **23** → **24** + **25**), and rearrangement to give the diamantane skeleton (**13**, **14** → **2**). This method is general, and could in principle be used to elaborate any lower diamondoid hydrocarbon to a higher one.

Polycycloalkanes with diamond lattice structure generally possess ultimate thermodynamic stabilities.[2] Consequently, Lewis acid catalyzed carbocationic isomerizations provide remarkably successful syntheses of many molecules of this type,[2] e.g., adamantane (**1**),[3] diamantane (**2**),[4] and, in lower yield, triamantane (**3**).[5]


1


2


3

However, an attempt to prepare a tetramantane by this route failed; instead, isomerization of a $C_{22}H_{28}$ precursor led to "bastardane", a compound with an irregular rather than a diamondoid structure.[6] This result demonstrates that thermodynamic control cannot always be realized, owing evidently to high barriers for certain of the rearrangement steps when the dihedral angles are unfavorable[7] or to the required involvement of high-energy intermediates.

A viable synthetic alternative might be to elaborate a more readily available lower diamondoid hydrocarbon (e.g., adamantane, **1**) to a higher one (e.g., diamantane, **2**) by adding four new carbons and two new rings. We have developed such a general procedure which should permit the synthesis of unknown higher polyamantanes.[8]

Synthetic Design and Results

Our objective was to convert adamantane (**1**) to diamantane (**2**) in a stepwise manner. The first part of the synthesis [ac-