Anal. Calcd for $C_{23}H_{10}O_2N_4$: C, 73.77; H, 2.67; N, 14.42. Found: C, 73.70; H, 2.70; N, 14.51.

Reaction of 3 with Oxabenzonorbornadiene (28). A solution of **3** (246 mg) and oxabenzonorbornadiene (**28**, 144 mg) in chlorobenzene (4 ml) was heated in a sealed tube at 100 °C for 11 h. Evaporation to dryness and chromatography on silica gel using benzene–chloroform (1:1) gave a 1:1 adduct (**29**, 330 mg, 85%), mp 250–252 °C (benzene–$CHCl_3$).

Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 83.24; H, 4.51.

Reaction of 3 with Isobenzofuran (1a). A solution of the 1:1 adduct[9] of **28** and tetracyclone (275 mg) and **4** (136 mg) in *p*-xylene (10 ml) was heated in a sealed tube at 170 °C for 1 day. Workup as described above gave compound **30** (50 mg) and **31** (55 mg) (total yield of 54%), and 1,2,3,4-tetraphenylbenzene (190 mg, 99.4%).

30: mp 294–295 °C ($CHCl_3$).

Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 82.96; H, 4.94.

31: mp > 300 °C ($CHCl_3$).

Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 82.99; H, 4.70.

Registry No.—1a, 270-75-7; **3,** 20457-17-4; **4,** 16567-36-5; **5,** 6830-78-0; **6,** 891-22-5; **7,** 622-37-7; **8,** 817-87-8; **11,** 479-33-4; **12,** 26307-17-5; **13,** 2207-27-4; **14,** 5471-63-6; **15,** 58241-44-4; **16,** 58241-45-5; **17,** 58241-53-5; **18,** 58241-46-6; **19,** 58241-52-4; **20,** 941-69-5; **21,** 106-51-4; **22,** 762-42-5; **23,** 670-54-2; **24,** 58241-47-7; **25,** 58241-48-8; **26,** 58241-49-9; **27,** 58241-50-2; **28,** 573-57-9; **29,** 58241-51-3; **30,** 58267-64-4; **31,** 58267-65-5.

Supplementary Material Available. Tables I and II, NMR data (2 pages). Ordering information is given on any current masthead page.

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Gas Phase, Uncatalyzed Thermolysis of 3-Homoadamantyl Acetate

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3-Homoadamantyl acetate has been shown to undergo unimolecular gas phase thermolysis with $E_a = 48.1 \pm 0.4$ kcal/mol. The variation in product distribution with temperature, and upon 4 deuteration, has been taken as evidence for parallel pathways of thermal decomposition. A mechanistic scheme has been proposed involving competition of well-precedented six-membered and seven-membered transition states giving rise to two products (**3** and **4**) and one unique product (**2**), respectively. Moreover, substrates, such as **8** and **9**, which are structurally incapable of realizing a low energy seven-membered or a six-membered cyclic pathway which does not result in bridgehead olefin formation, seem to be completely stable under conditions which lead to extensive decomposition of **1**. However, the formation of an exocyclic cyclopropane at a bridgehead or an equivalent (relatively) stable diradical leading to **2a** or **2b**, stemming from the thermolysis of **1**, appears to take place readily via a seven-membered transition state.

Recently Kovacic and Adams[1] have disclosed that the gas phase thermolysis of 3-homoadamantyl acetate (**1**) in a Vycor (quartz)-packed reactor tube at 500–600 °C produces two olefinic products in a combined yield of ca. 30–40%, accompanied by a host of other products, each in very small amounts. Their report was particularly intriguing because the predominant products, 4-methyleneprotoadamantane (**2**) and 3-vinylnoradamantane (**3**), obtained in a ratio of ca. 2.5:1, obviously resulted from skeletal rearrangements.

We have for some time been interested in the course of the normal, six-centered, retroene thermolysis reaction by which the usual, unrearranged olefins are formed, as well as that of the less common thermolysis from which only rearranged products originate through the operation of a seven-centered or homoretroene pathway.[2] The data of Kovacic and Adams,[1] who did not provide any mechanistic interpretation, indicated that the relative quantities of **2** and **3** in the complex product mixture varied somewhat. This suggested the possibility that the multiplicity of products may arise from either a competition of reaction mechanisms or rate-determining formation of a common intermediate with more than one rapid, product-forming pathway available to it. In the search for evidence to elucidate the reaction routes producing **2** and **3**, under highly reproducible, noncatalytic, thermolysis conditions, a kinetic investigation of the thermolysis of **1** and related substrates was undertaken.

Results and Discussion

In contrast to the preparative scale, quartz-packed, hot tube previously employed[1] the kinetic studies of interest were carried out with a micro, gas phase, flow system utilizing a gold-coil reactor which has been established[3] to minimize or eliminate the wall-catalyzed reactions commonly found to take place in glass or quartz reactors. This system has been shown to exhibit even less catalytic activity in ester thermolysis than the well-seasoned reactor of Maccoll[4] which is most widely employed[5] as a means of *diminishing* the recognized catalytic activity of glass and quartz-based reactors.

The thermal decomposition of **1** studied in the gold-coil microreactor over the temperature range 445–500 °C followed a simple, unimolecular rate law. The rate data gathered from these measurements are compiled in Table I. In sharp contrast to the results obtained[1] with the use of the (apparently) catalytic Vycor reactor in the temperature range of 500–600 °C, only three, clean products are ob-

Table I. Gas Phase Thermolysis of 3-Homoadamantyl Acetate in the Gold Coil Microreactor

Temp, °C[a]	Rate, s^{-1} [a]	
497	1.09; 1.10	$E_a = 48.1 \pm 0.4$ kcal/mol
488	0.75; 0.74	$\log A = 13.67 \pm 0.16$
476	0.46; 0.47	$\Delta S^{\ddagger} = 0.2 \pm 0.6$ eu
466	0.28; 0.28	
455	0.18; 0.17	$k = \frac{-\log C/C_0}{t}$ where C = concn of 3-homoadamantyl acetate; C_0 = initial concn
445	0.11; 0.11	

[a] Temperatures and rates rounded off after least-squares analysis.

served here at some 50–150 °C lower temperatures. Within the limits of GLC (6 ft, 5% UCW-98 on Chromosorb W AW, 70–225 °C, 20 °C/min, *o*-dichlorobenzene internal standard) detection, small side products (<1%) are completely absent in the effluent of the gold-coil microreactor. The first and second product peaks were indeed identical with those previously reported, respectively, the (vinyl) **3** and (methylene) **2** products. The third product peak, predicated on the basis of a seven-centered transition state, was identified as 4-homoadamantene (**4**). The proportions of products **3** and **4** relative to **2** increase somewhat in proceeding from the lowest to the highest temperatures of study. Since these products were shown to be stable under the reaction conditions, the results are consistent with **1** decomposing via two parallel paths having activation parameters of comparable magnitudes. While the activation parameters are not abnormally large (i.e., close to $E_a = 48$ kcal), they are more characteristic of the decomposition of a secondary rather than of a typical tertiary acetate; *tert*-butyl acetate is given variously as $E_a = 40.5$–42.1 kcal.[6]

The occurrence of two parallel pathways of decomposition of **1** is supported by evidence obtained in thermolysis of 4,4-dideuterio-3-homoadamantyl acetate (**1**-*d*). Under identical reactor conditions the proportions of **3** and **4** maintained the same ratio with respect to each other as they had in the product composition arising from the protio substrate **1**. Moreover, a comparison of the rate constants for unimolecular decomposition of the protio (**1**) and deuterio (**1**-*d*) substrates at 477 °C ($k_H = 0.47$ and $k_D = 0.34$ s^{-1}) affords a clear indication of a primary kinetic deuterium isotope effect;[7] that is to say, the thermolysis process can be identified as one in which hydrogen transfer is occurring in a transition state similar in structure to that of the cyclic, symmetrical activation step for six-centered retroene, thermolysis mechanisms.[8]

This conclusion can be reached when the data are analyzed in the following way.

Parallel Reaction Pathways[9a]

$$1 \xrightarrow{k_1} 2$$

$$1 \xrightarrow{k_2} 3 + 4$$

Since $k_H^{477\ °C} = 0.47$ and $k_D^{477\ °C} = 0.34$, and at 477 °C for a symmetrical transition state $k_H/k_D = 2.1$,[7] and since only the *sum* of components **3** + **4** is diminished by 4 deuteration, then at this temperature

$$k_1 + k_2 = 0.47 \qquad \text{for } \mathbf{1}$$

$$k_1 + \frac{k_2}{2.1} = 0.34 \qquad \text{for } \mathbf{1}\text{-}d$$

Thus, $k_1 = 0.22$ and $k_2 = 0.25$ s^{-1} for decomposition of **1** at 477 °C; from these values it is computed that the product composition should consist of 47% of **2** and 52% of **3** + **4**, in close agreement with experimental observation. The GLC shows the peak of **3** well resolved and equal to 30% of the total product. The peaks of **2** and **4** are partly overlapped and for most purposes cannot be completely separated. Nonetheless, the computation above confirms that **4** is formed to the extent of 22% in the decomposition of **1**.

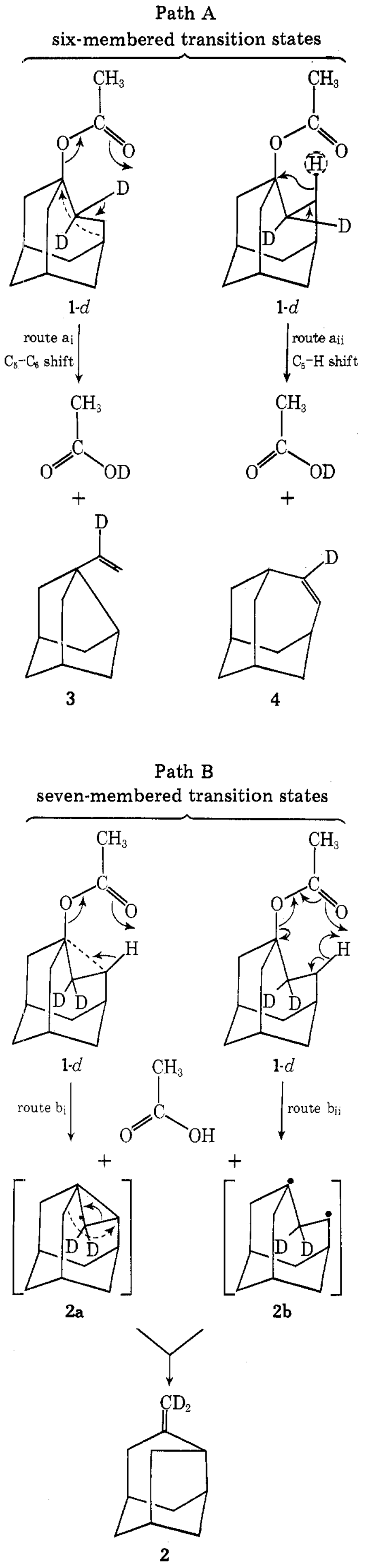
For the deuterio analogue **1**-*d* the decomposition rate constants are calculated to be respectively $k_1^D = 0.22$ and $k_2^D = 0.12$. The calculated proportions of the products on this basis are respectively **2**-*d* 63%, **3**-*d* 21%, and **4**-*d* 16%. This is in close agreement with the most accurate (GLC) determination of the well-resolved, deuterated product **3**-*d* = 22%. These results can be readily construed to support symmetrical, concerted transition states[8] for both (k_1 and k_2) pathways of hydrogen transfer in the gas phase thermolysis of 3-homoadamantyl acetate.

An attractive way of representing these concerted pathways of decomposition, each involving skeletal rearrangements, is given in Chart I. Path A involves concerted hydrogen (deuterium) abstraction in a six-centered transition state accompanied by two nearly equally probable rearrangements: (1) delocalization of the C_5–C_6 bond via route a_i, (2) migration of the C_5 hydrogen to C_3 in synchronism with the departure of the C_3–oxygen bond via route a_{ii}. Path B depicts a seven-centered transition state reminiscent of one identified for the thermal rearrangement of neophyl esters.[2a,b] It involves here, however, the transient formation of a strained cyclopropane structure which may be presumed to rearrange spontaneously[9b] (as shown by route b_i) to the observed olefin **2**.

A mechanistic alternative involving formation of the bridgehead olefin intermediates, 2- and 3-homoadamantenes (**6** and **7**, respectively), can be visualized with the aid of the reaction scheme[9c] depicted in Chart II. An initial rate-determining, concerted, six-centered elimination is drawn to produce the highly strained products **6** and **7**, with **7** designated as the precursor of approximately 60% of the observed product composition. While this may appear to be also a very eligible and even an attractive interpretation of the results obtained here with the gold-coil microreactor, serious reservations come to mind upon detailed consideration of the data.

First it must be emphasized that thermolysis of **1** in the gold-coil microreactor occurs with an activation energy similar to what is normal for formation of unstrained olefins via (uncatalyzed) cyclic, concerted, transition states of thermolysis, which, by definition, reflect the product energies. The well-grounded hypothesis of Wiseman[10] guides us to the conclusion that a cyclic concerted transition state leading to the bridgehead olefins **6** and **7** should reflect, respectively, the very high strain energies of *trans*-cycloheptene and *trans*-cyclohexene. The results of Allinger[11] using molecular mechanics procedures have verified by these methods the approximately 20 kcal of excess strain energy in *trans*-cycloheptene compared to the stable cis isomer, and for *trans*- vs. *cis*-cyclohexene 42 kcal. It can therefore

Chart I



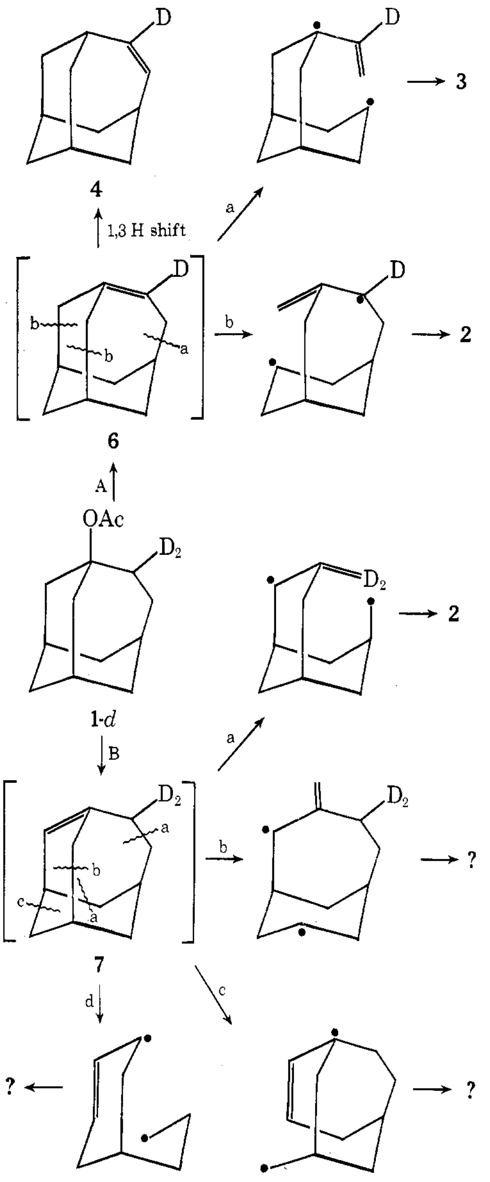
Path A

six-membered transition states

Path B

seven-membered transition states

Chart II



be deduced that a concerted reaction process leading to the bridgehead olefins **6** and **7**, as pictured in Chart II, should involve activation energies which could be as much as 20–40 kcal higher than corresponding reaction mechanisms producing unstrained olefins. Since the observed thermolysis of **1** in the gold-coil microreactor takes place with activation parameters which are normal for the formation of (say) propylene from isopropyl acetate, the mechanism of Chart II does not seem appropriate.

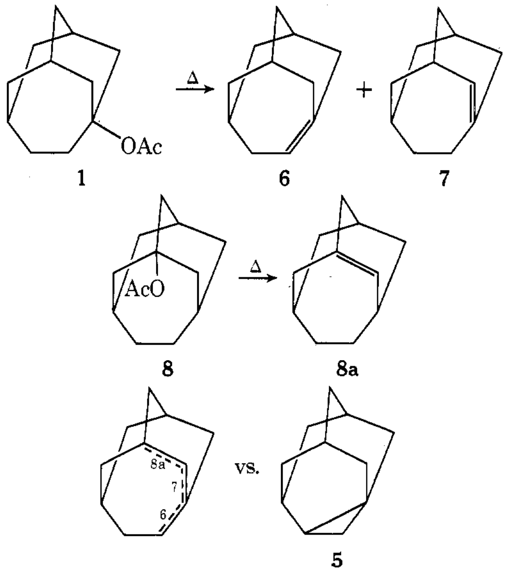
Secondly, the nature and magnitude of the kinetic deuterium isotope effect is consistent with the six-membered, concerted transition states of rearrangement proposed for the routes (a_i) and (a_{ii}) shown to produce **3** and **4** in Chart I. The approximately 6–7 kcal increase in E_a compared to *tert*-butyl acetate thermolysis seems to be a reasonable increment of energy necessary to effect the rearrangement step. It is of no greater magnitude than the E_a distinguishing the thermolysis of ordinary secondary and tertiary acetates.

The third reaction pathway (route b_i) by which product **2** originates seems at first glance to be of surprisingly low E_a, since it is shown to involve formation of a strained bridgehead cyclopropane at an energy level which is characteristic of the formation of unstrained olefins. It is conceivable that the greater stability of benzocyclopropene (an isolable intermediate compared to benzyne[12]) provides some justification for the assumption of far greater stability for a transient bridgehead cyclopropane with the strain energy of the *trans*-bicyclo[5.1.0]heptane intermediate **5** than for the *trans*-cycloheptene of which the bridgehead structure of **6** is constructed.[10]

On the other hand, it may not be necessary to assume formation of a transient cyclopropane in route b_i if this pathway is not fully concerted. Under such circumstances in an alternative path (route b_{ii}) a diradical intermediate **2b** might be realized, in which the radical centers are stabilized at neighboring tertiary and secondary carbon centers geometrically accommodated for rearrangement into the observed product **2**.

Considerations on the Feasibility of Bridgehead Olefin and Bridgehead Cyclopropane Intermediates in Ester Thermolysis. In the effort to shed some light on the possible formation of a transient, bridgehead olefin during thermolysis of substrates like **1**, experiments were devised based on the following reasoning. If bridgehead olefin formation is not energetically unfeasible, at energy levels consistent with observations on **1**, then it *must be* assumed that 2- and 3-homoadamantenes, though possessing respectively the very different energies[10] characteristic of *trans*-cyclohexene and cycloheptene, *nonetheless are equally stable. This assumption is imperative to be consistent with the fact that increasing E_a by ca. 1.1 kcal through introduction of deuterium (in* **1-d**) *is observed to change the product mixture considerably.* This assumption therefore anticipates that 1-homoadamantyl acetate (**8**) must undergo rate-determining thermolysis to the homoadamantene **8a** (Chart III) under comparable conditions and with approximately the same ease attending the decomposition of **1**. According to the mechanistic scheme of Chart II the formation of the bridgehead olefin **7** must be involved to account for some 60% of the observed product composition. Since **7**, like the putative product **8a**, is a bridgehead *trans*-cyclohexene strained olefin,[10] the activation requirements for formation of **7** and **8a** (i.e., the E_a for thermolysis of **1** and **8**) should be expected to be very similar.

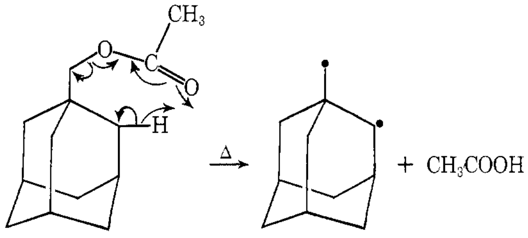
Chart III. View of Bridgehead Possibilities in Various Homoadamantenes



On the other hand, the decomposition of **8** is structurally excluded from taking place via cyclic, concerted pathways similar to those outlined in Chart I, i.e., pathways presumably of lower activation requirement than those involving bridgehead olefin intermediates. Consequently, **8** can be expected to be stable under conditions which cause **1** to undergo extensive thermolysis, since bridgehead olefin formation cannot be avoided in the course of an uncatalyzed decomposition of **8**. In this connection it is found that, for a residence time during which 50% decomposition of **1** has taken place at 485 °C, **8** *is completely unreacted.* Moreover, for the same residence time in the gold-coil reactor, a temperature of 600 °C is necessary to effect the disappearance of 50% of **8**, fully 100 °C above the maximum temperature required for practically complete decomposition of **1**. That is to say, an activation energy some 12 kcal greater than for **1** is necessary to produce thermolysis of **8**, a reaction which (if it can only occur via a cyclic concerted mechanism) must result in the transient formation of a bridgehead olefin. As a result of these data it may be said that the mechanistic course depicted in Chart II is improbable.

Finally, some consideration was given to the course of thermolysis of adamantylcarbinyl acetate[13] (**9**). Under solvolytic conditions[14,15] this substrate can be involved in a mobile equilibrium with the homoadamantyl substrate **1**. However, when subjected to thermolysis at temperatures up to 600 °C it would appear that **9** does not have available to it the facile pathways for cyclic concerted thermal decomposition established by the results obtained with **1**. At these temperatures, for short dwell times in the flow reactor at which **1** is completely decomposed, **9** shows unusual resistance. In excess of 600 °C where decomposition does begin to occur, only the formation of a large number of unidentified products believed to arise from various homolytic bond cleavages is observed to take place.

This observation may be of considerable significance in assessing the feasibility of the routes b_i and b_{ii} leading respectively to product **2**. Thus, if **9** could undergo a low-energy, retroene transition state of thermolysis similar to that considered in route b_i (Chart I) it should produce the same cyclopropane intermediate. The observed failure to achieve this result could be due to either of two causes: (a) the substrate **9** undergoes the route b_i decomposition, corresponding to the transition state of a primary acetate thermolysis whose E_a is usually at least 7 kcal higher[6] than for corresponding tertiary acetates; or (b) both **1** and **9** possess the geometric requirements for forming a diradical intermediate via a nonconcerted pathway, but the diradical **2b** leading from **1**, having a tertiary radical center, is considerably more stabilized than **2c** leading from **9** and having a corresponding unstable primary radical center (which is at least 6 kcal less stable[16]).



Experimental Section

1-Adamantylcarbinyl acetate was prepared according to the procedure of Norlander et al.,[14] bp 110–112 °C (2.5 mm) [lit.[14] bp 110–113 °C (2.5 mm)].

1-Adamantyl-1′,1′-dideuteriocarbinyl tosylate was prepared according to the method of Stetter et al.[17] except that 1-adamantyl-1′,1′-dideuteriocarbinol (from the lithium aluminum deuteride reduction of 1-adamantylcarboxylic acid) was used, mp 78.0–78.5 °C (lit.[14] mp 76 °C).

4,4 Dideuterio-3-homoadamantyl acetate was prepared according to the method of Schleyer et al.[14,15]

1-Homoadamantyl acetate was prepared from a sample of 1-homoadamantanol kindly provided by S. Godleski and P. v. R. Schleyer.

Registry No.—1, 14504-81-5.

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Syntheses of the Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecyl (Trishomocubyl) and Tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undeca-2,6-dienyl (Homohypostrophenyl) Systems[1]

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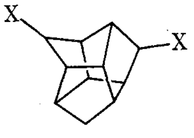
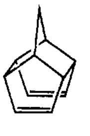
Acid-catalyzed rearrangement of the diol **6** obtained from the product of photocyclization of the *p*-benzoquinone–cyclopentadiene Diels–Alder adduct produces the C_3-symmetrical trishomocubane system. Diiodotrishomocubane (**1c**) produced either directly from **6** or by a sequence via bistosylate **1f** provides a good source of the diene homohypostrophene (**2**) by reductive dehalogenation. The hydrocarbon trishomocubane (**1a**) can be obtained in high yield from the diiodide **1c** by reduction with metallic zinc under acidic conditions.

Several reports in the recent literature have dealt with the syntheses of the closely related trishomocubyl (**1**) and homohypostrophenyl (**2**) systems. The unsubstituted hydrocarbon **1a** has been produced by reductive dehalogenation of dibromotrishomocubane **1b** as one of a mixture of products,[2a] by zinc–acetic acid reduction of the diiodide **1c**,[2b,c] and by Wolff–Kishner reduction of trishomocubanone (**3**).[3a] The monofunctional trishomocubanone (**3**) was obtained in a four-step sequence starting with the dione produced by ultraviolet irradiation of the *p*-benzoquinone–cyclopentadiene Diels–Alder adduct,[3a] as well as by decomposition of an organometallic intermediate derived from the photocyclization product of dicyclopentadiene.[3b] The diene **2**, which had been required for the synthesis of the first-reported[2a] trishomocubane structure, had been observed as a by-product in the attempted synthesis of homopentaprismane (**4**) from the dibromide **5**.[4] Homohypostrophene (**2**) was also obtained as a minor component of the



1a, X = H
b, X = Br
c, X = I
d, X = OAc
e, X = OH
f, X = OTs



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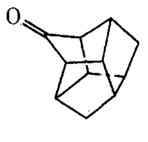

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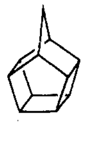

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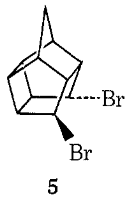

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