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Rearrangement during Thermal Decomposition of 3-Homoadamantyl Acetate[1]

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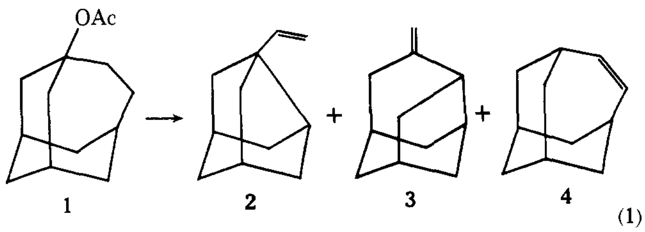
Abstract: Pyrolysis of 3-homoadamantyl acetate provided 3-vinylnoradamantane, 4-methyleneprotoadamantane, and 4-homoadamantene in the approximate ratio, 30:65:5. Reaction was performed at 470-600° with varying flow rates. Ozonolysis and hydrogenation were carried out with the major products. Addition of formic acid and acid-catalyzed polymerization involving 4-methyleneprotoadamantane apparently proceeded with rearrangement to the adamantyl nucleus. Thermolysis of 4,4-dideuterio-3-homoadamantyl acetate provided a primary deuterium isotope effect of 2.3, in addition to other mechanistic insight. Ester decomposition is believed to proceed via a six-membered cyclic transition state.

In connection with our interest[4,5] in the limits of Bredt's rule in caged tricyclic systems, we have investigated the decomposition of 3-homoadamantyl acetate (**1**). There has been considerable, recent activity aimed at the generation of bridgehead olefins.[6-9] Various techniques have been used to produce highly strained alkenes, including Hofmann elimination,[6] bisdehalogenation of vicinal dihalides,[7] rearrangement of bridgehead carbenes,[8] and perester thermolysis.[9c] However, we have found no reports[10] on the decomposition of bridgehead esters to give "anti-Bredt's rule" olefins.

Gas-phase pyrolysis of esters is generally used to introduce a double bond without isomerization. Rearrangement is not usually observed except in the absence of a β hydrogen or the presence of a cerain type of cyclic structure.[11] With the homoadamantyl system, it was anticipated that decomposition of **1** might take place with intermediate formation of bridgehead olefin or with concerted rearrangement.

Results and Discussion

Pyrolysis of 3-homoadamantyl acetate[12] (**1**) afforded 3-vinylnoradamantane (**2**), 4-methyleneprotoadamantane (**3**), and 4-homoadamantene (**4**) in combined yields of 30-60% (eq 1). The relatively low yield reflects, in part, losses from trapping and work-up with the small scale runs. It is pertinent that doubling the yield (30 → 60%) did not significantly alter the product composition. No more than very small amounts of a few other, unidentified products were present according to GLC. The olefins amounted to approximately 85% of the collected product, with the remainder consisting of material nonvolatile under GLC conditions. The ratio **3**:**2** varied in the range of 2-3:1 depending on flow rate at temperatures of 500-600°, while **4** comprised only a few percent of the product, decreasing with increasing temperature. The conditions entailed passage of the vapor (ca. 2 g) during 2 to 4 hr through a Vycor tube containing Vycor chips at 470-600° with nitrogen as the carrier gas. The flow rate of the nitrogen was approximately 3-9 l./min.



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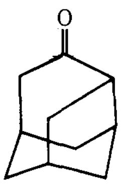
The structures of the olefins were determined by NMR, ir, mass spectral, and elemental analysis. In addition, comparison was made with authentic materials in the case of **3** and **4**. As an alternate route, the Wittig reaction was used to synthesize olefin **3** from ketone **5**. Treatment of the carbonyl compound with ylide, $Ph_3P^+CH_2^-$, afforded the desired alkene in only 10% yield.

Further verification was provided by chemical behavior. Olefins **2** and **3** were transformed by ozonolysis to the known ketone, 4-protoadamantanone[13] (**5**), and 3-noradam-



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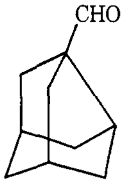

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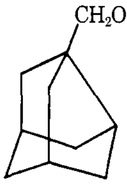

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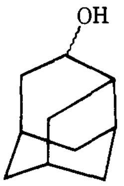

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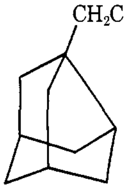
antanecarboxaldehyde (**6**). Reduction of the carbonyl-containing mixture with $LiAlH_4$ provided a known derivative of the aldehyde, 3-noradamantylcarbinol[14] (**7**), and the isomeric 4-hydroxyprotoadamantane[15] (**8**).

Hydrogenation of the olefin mixture over Pd on charcoal was also investigated. The corresponding hydrocarbons **9** and **10** were produced, with **10** consisting of a mixture of



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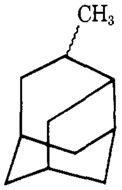

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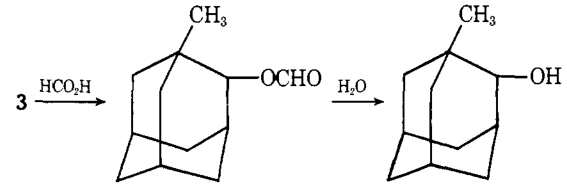
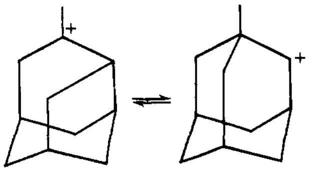
exo and endo isomers (1:4.7). The major isomer was assigned the endo configuration by analogy to hydride reduction of 4-protoadamantanone[15] (**5**). In the earlier work,[15] the endo isomer was favored by about 2:1. Presumably steric hindrance is quite pronounced in catalytic hydrogenation.

Ionic reactions of 4-methyleneprotoadamantane (**3**) are of particular interest because of facile rearrangement of the protoadamantyl to the adamantyl system.[15,16] A similar transformation has been observed[14] on treatment of 3-noradamantylcarbinol (**7**) with acid, which provides 1-adamantanol. However, this rearrangement appears to occur more readily with **3** than with the noradamantyl system. Treatment of pure **3** with formic acid in ether at reflux gave the rearranged product **11**. The mechanistic aspects are presumably analogous to those for the acid-catalyzed rearrangement of 4-methylprotoadamantan-4-ol to 1-methyladamantan-2-ol[15] (**12**). Protonation of the olefin or the alcohol leads to the tertiary cation which rearranges to the thermodynamically more stable adamantyl form (eq 2)



11 **12**

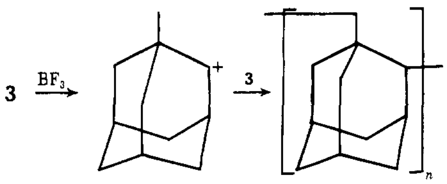


(2)

which then combines with water or formate ion. Some evidence has been presented for involvement of a bridged intermediate in eq 2.[16b-d] The absence of protoadamantyl product can also be rationalized by this approach since the 2-adamantyl cation appears to be the major contributor. Hydrolysis of ester **11** produced the corresponding alcohol **12**.

Under identical conditions with formic acid, olefin **2** remained unaltered. On treatment of the olefin mixture with 50% sulfuric acid at 35° for 6 hr, unchanged **2** was recovered, whereas **3** was completely converted to 1-methyladamantan-2-ol (**12**) under these conditions.

An interesting polymerization was observed with **3**, which presumably involves a similar acid-catalyzed rearrangement. Apparently, cationic attack occurs on 4-methyleneprotoadamantane (**3**) to form the tertiary carbonium ion which quickly rearranges to the more stable skeletal



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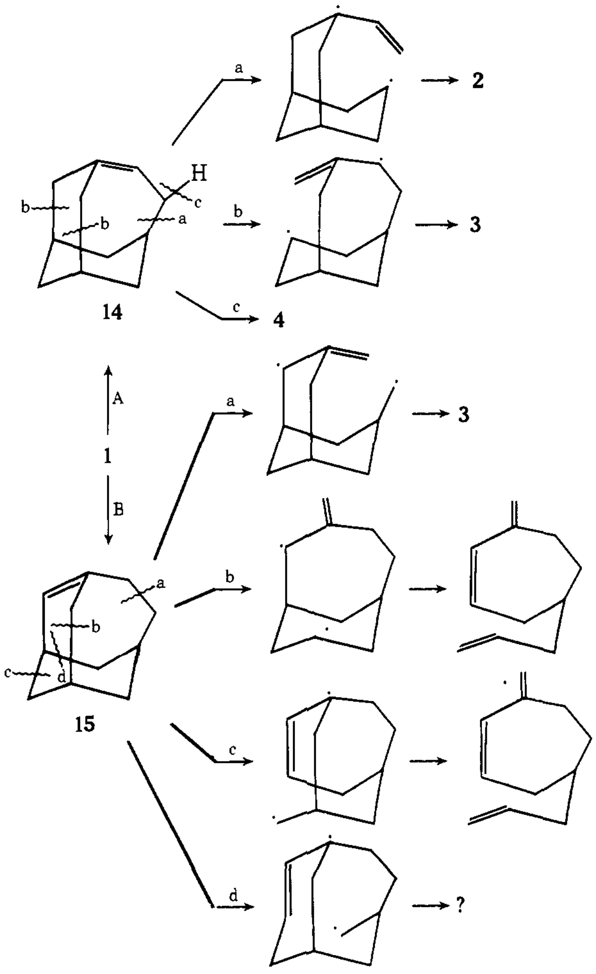
(3)

structure (eq 3), followed by propagation with **3**. The end result is the polymer **13**. Structural assignment was based primarily on NMR data.

The mechanism of pyrolysis of 3-homoadamantyl acetate is of particular interest in relation to Bredt's rule. There are several plausible pathways by which elimination might take place. First, rearrangement may occur in a concerted fashion with elimination such that an unsaturated intermediate is not generated at the bridgehead. Another possibility is that strained bridgehead olefins, **14** and **15**, might form initially and then rearrange at the high temperatures to the observed products. We wish to emphasize that our basic premise entails a six-membered cyclic transition state; at present, the data do not permit a clear choice between the concerted and alkene routes. For each of these mechanisms, there are two elimination pathways and several possible rearrangements (Scheme I).

Scheme I



Abstraction of a hydrogen from the longer bridge gives product via path A. Cleavage of bond "a" yields 3-vinylnoradamantane (**2**). Breaking either bond "b" results in formation of 4-methyleneprotoadamantane (**3**). The 1,3 migration of a hydrogen atom, path c, gives 4-homoadamantene (**4**). If acetic acid is eliminated from either of the shorter bridges, product would arise from path B rearrangements. Four different allylic bond cleavages or rearrangements are possible. Breaking bond "a" results in formation of **3.** Cleavage of either bond "b" or "c" gives similar intermediates which require additional allylic bond breakage to form stable products. If reaction occurs at bond "d", multiple σ-bond cleavage must result if a stable product is to form. The intermediate diradical cannot readily react intramolecularly since this would result in unlikely geometry at the bridgehead carbon; i.e., all bonds would be directed to one side of a plane containing the tetrahedral carbon.

Since these rearrangements (b-d) are energetically less favored than "a", i.e., they entail cleavage of more σ bonds to form π bonds, and since no products arising from these rearrangements (b-d) were isolated, we postulate that elimination via path B leads almost exclusively to **3.**

In a unimolecular reaction, the most important aspect would be the statistical probability of hydrogen abstraction unless pronounced steric, electronic, or thermodynamic factors pertain.[11,17] Models show that all the hydrogens are in a favorable position to form the cyclic six-membered transition state which is proposed[11,17] for ester elimination. It is apparent that electronic factors will not affect the direction of elimination, nor are there any bulky groups to interfere.

The major factor which can overcome the directional influence of the statistical probability in Scheme I is the thermodynamic stability (strain) associated with the postulated alkene intermediates. In the nonconcerted mechanism, the stability of 3-homoadamantene (**14**), path A, should be substantially greater than that of 2-homoadamantene (**15**), path B. This will be reflected in product distribution being favored from path A, rather than path B. In the concerted mechanism of Scheme I, if there is no appreciable strain in the transition state, the probability factor in hydrogen abstraction would play an important role favoring path B over path A.

Several experiments involving investigation of reaction variables were carried out. Pyrolyses were run at varying temperatures and nitrogen flow rates (Table I). There is a noticeable increase in the ratio of **4**:(**2** + **3**) with decrease in temperature. One would expect the yield of **4** to increase substantially beyond 6% with further decrease in temperature and use of a smaller reactor. The data indicate that, at constant flow, the ratio of olefin **3** to products **2** plus **4** is essentially constant over the temperature range of 500-600°. Changing the flow rate at constant temperature (550°) alters this ratio only slightly, in favor of **3.** This slight change in the ratio, if actually outside experimental error, may be reflective of the relative stabilities of the two products or may be indicative of a small amount of heterogeneous catalysis. Pyrolysis of the olefin mixture at 600° demonstrated that **3** was destroyed at a somewhat faster rate than **2.** At 500°, the relative rate of decomposition was essentially the same. Pyrolysis of **1** at 550° without Vycor packing gave a ratio of **3**:(**2** + **4**) of 2.3 (vs. 1.9 with packing). Some increase in the ratio with the empty tube would be expected because of the greater thermal lability of **3** vs. **2.** This observation indicates that wall effects play only a minor role. Several other considerations point to the essential absence of catalysis. When wall effects occur, they are known to be eliminated or minimized by continued use (seasoning).[11] We observed no significant changes in product composition or yields after many pyrolyses were carried out. Literature reports[11] show that gross changes in quantity and nature of products can occur when wall effects intrude. It is quite significant that results from the Vycor and gold-coil[18] (zero wall effect) reactors are strikingly similar, taking into consideration the differences in temperature, residence time, and isolation procedure.

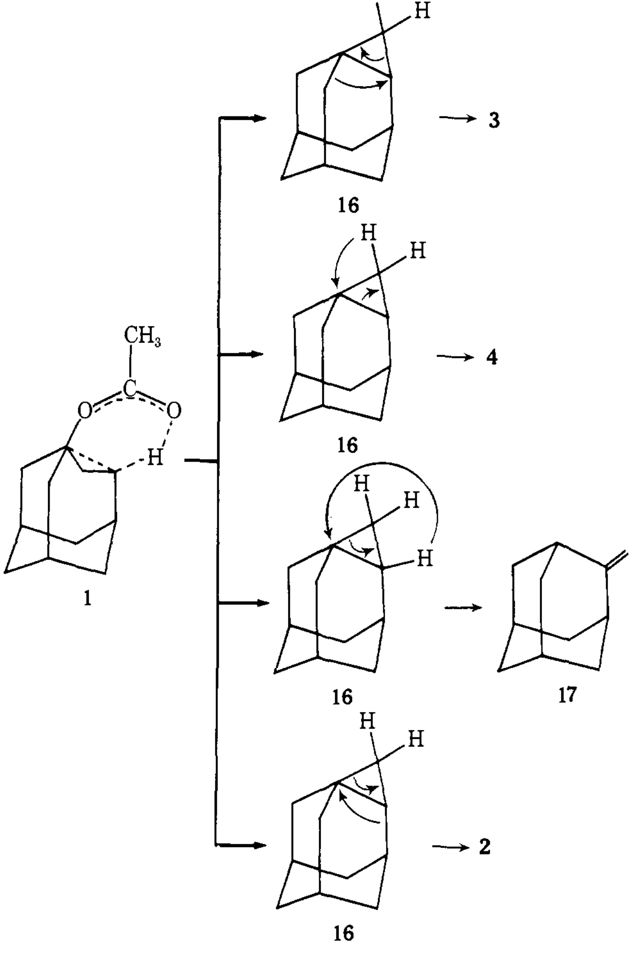
Table I. Pyrolysis of 1 at Various Temperatures and Flow Rates

Temp	Flow rate, l./min	Relative % 2	3	4	Ratio of 3 : (2 + 4)
470	9.6	34	60	6	1.6
500	3.2	27	67	6	2.0
520	3.2	30	65	5	1.9
540	3.2	31	65	4	1.9
550	3.2	32	66	2	1.9
550	9.6	29	69	2	2.2
580	3.2	33	65	2	1.9
600	3.2	32	67	1	2.0
550[a]	3.2	29	70	1	2.3
500[b]	3.2	16	81	4	4.1
500[b]	3.2	19	77	4	3.4
550[b]	3.2	22	76	2	3.2
550[b]	3.2	18	81	2	4.1

[a] Pyrolysis without Vycor chip packing. [b] Reaction of 1-d_2.

Another mechanistic possibility, advanced by Kwart[18,19] for certain cases of ester decomposition, involves a concerted, cyclic, seven-membered transition state. Application (Scheme II) to the present case would entail formation of 3,5-dehydrohomoadamantane (**16**) followed by subsequent rearrangement. Intermediate **16** can serve as precursor to all of the observed products. However, there was no evidence for generation of 2-methyleneadamantane (**17**).

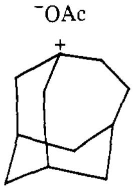
Scheme II



In the hypothesis involving **16**, steric factors would seem to be quite influential. Models indicate that the appropriate hydrogen in the 5 position would be in an unfavorable geometry for abstraction, with adverse steric interactions existing between the carbonyl and H-4. Apparently, the carbonyl oxygen and the ethylene bridge must be in a very constrained position in order to attain the requisite seven-membered cyclic transition state. Therefore, this comprises one factor which argues against this mechanism in comparison to Scheme I. There is little basis for preference between **14** and **16** on steric grounds since both intermediates would be highly strained.

Neophyl acetate, which has been postulated[19] to decompose via a seven-membered transition state, undergoes reaction to the extent of only 6% at 550° and 19% at 600°. In marked constrast, acetate **1** is decomposed completely at 550° in our system, yet the migrating group is alkyl as opposed to phenyl in the neophyl substrate. On the other hand, the R groups differ in nature in the two systems, neopentyl type vs. bridgehead tertiary.

Thermolysis of 1-adamantylcarbinyl acetate (**18**) was investigated, which is pertinent to the question of possible ester rearrangement during thermolysis of **1**, as well as to the hypothesis of a seven-membered, cyclic transition state for **1**. When **18** was pyrolyzed at 600°, analysis revealed that the condensed effluent was made up predominantly of unchanged acetate (97%), with most of the remaining material consisting of olefins **3** and **2** in a ratio of 2.85. It is apparent that **18** is not rearranging to **1** to any important extent. The very high degree of stability of **18** at high temperatures convincingly demonstrates that reaction of **1** does not significantly entail a pathway leading initially to the ion pair (**19**) which rearranges to **18** followed by decomposition to end products. Furthermore, **18** was not detected by GLC in the product mixture from **1**, indicating that the homoadamantyl-adamantyl carbinyl rearrangement is not a favored process, but may account for the small amount of observed reaction. Acetate **18** possesses no β hydrogens and, hence, cannot undergo decomposition by the usual ester pyrolysis pathway. It can, however, eliminate via a seven-membered or five-membered cyclic transition state (Scheme III). The seven-membered pathway is similar to that for **1**, Scheme II, both yielding **16**. Formation of the bridgehead olefin **14** might occur by α elimination, as has been postulated by Kwart for the neophyl system.[20] Alkene **14** would be expected to give products as illustrated by path A in Scheme I. These results raise further doubts concerning the appropriateness of a seven-membered transition-state for **1**. However, the enhanced thermal stability of acetate **18** vs. **1** might also be explained on the basis of the difference in reactivity between primary and tertiary esters. The small amount of olefins generated from the Vycor reactor may result from heterogeneous catalysis.



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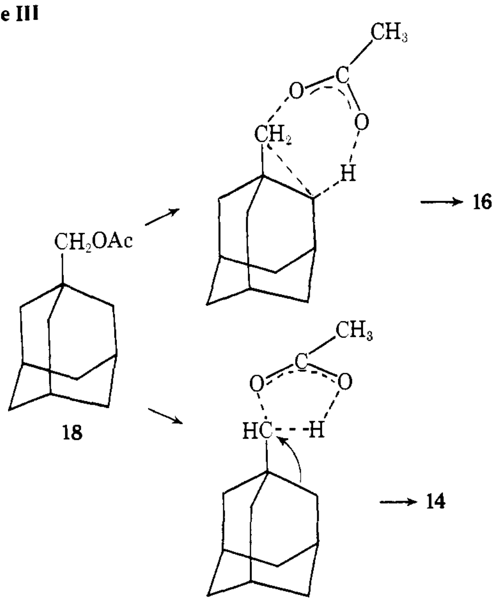
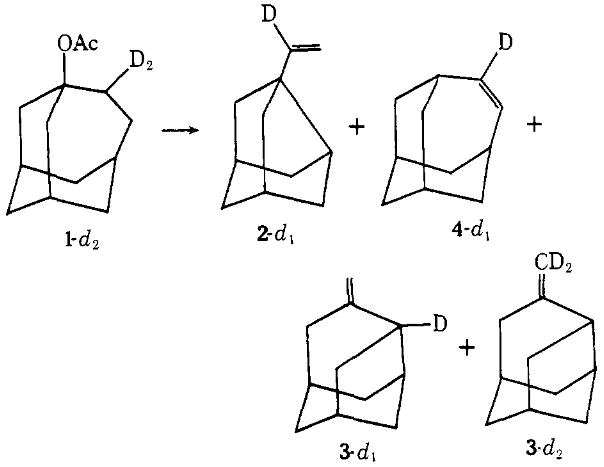
Scheme III



To determine the relative amounts of elimination via each pathway (A and B, Scheme I), the deuterated acetate was pyrolyzed. 4,4-Dideuterio-3-homoadamantyl acetate (**1**-d_2), synthesized by the same series of reactions as for **1** by substituting LiAlD$_4$ for LiAlH$_4$, was decomposed at 500 and 550° at constant flow rate. It can be seen from Table I that there is operation of a deuterium isotope effect based on the change in the ratio of **3**:(**2** + **4**). The two major olefins, **2** and **3**, were analyzed by NMR.[3] The vinyl pattern of **2** was in keeping with the presence of one atom of deuterium in the position illustrated in **2**-d_1 (eq 4). Instead of the ABX pattern of undeuterated **2**, an ill-resolved doublet was observed for the higher field protons, and essentially no absorption for the lower field hydrogen. Product **4**, which amounts to only a few percent of the total, was not completely characterized by mass spectral analysis. 4-Methyleneprotoadamantane (**3**) was found to contain both mono- and dideuterio olefins. NMR integration, involving comparison of the terminal methylene absorption to that of the ring protons, indicated relative amounts for **3**-d_1 and **3**-d_2 of 23 and 77%, respectively, at 500°, and 22 and 78%, respectively, at 550°. The deuterium distribution was further corroborated by mass spectral data. The findings that **2** and **4** are monodeuterated, and that olefin **3** is present in two deuterated forms (**3**-d_2 and presumably **3**-d_1) as predicted by Scheme I comprise very convincing evidence against the mechanism involving a seven-membered, cyclic transition state and are in complete accord with our proposal.



(4)

From the values for the relative amounts of **3**-d_1 and **3**-d_2, the relative rates of elimination via path A and path B can be calculated for the deuterated acetate, **1**-d_2, and the nondeuterated acetate, **1**. Table II lists the amounts of each product from **1**-d_2. Since in Scheme I the rearrangement pathways after elimination involve only a secondary deuterium isotope effect, which is negligible within experimental error, the ratio of **2**:**3** formed by path A will be essentially the same for deuterated and nondeuterated acetates. Hence, the quantity of alkene **3**-d_1 from path A can be used to calculate the amounts of **3** from either pathway for decomposition of **1**, even though they cannot be measured directly. The overall ratio of elimination for path A to path B may then be determined (Table II).

Table II. Determination of k^A/k^B

		Relative %				
Temp	Flow rate, l./min	**2**	**4**	**3** (Path A)	**3** (Path B)	k^A/k^B [a]
500[b]	3.2	16	3	17	64	1.1
500[b]	3.2	19	4	16	61	1.3
550[b]	3.2	22	2	17	59	1.4
550[b]	3.2	18	2	16	64	1.1
470[c]	9.6	34	6	32[d]	28[d]	5.1
500[c]	3.2	27	6	25[d]	42[d]	2.8
520[c]	3.2	30	5	28[d]	37[d]	3.4
540[c]	3.2	31	4	26[e]	39[e]	3.1
550[c]	3.2	32	2	26[e]	40[e]	3.0
550[c]	9.6	29	2	24[e]	45[e]	2.4
580[c]	3.2	33	2	27[e]	38[e]	3.3
600[c]	3.2	32	1	26[e]	41[e]	2.9
550[c,f]	3.2	29	1	24[e]	46[c]	2.3

[a] Equals 2A/B, corrected for the statistical effect. [b] Reaction of 1-d_2. [c] Reaction of 1. [d] Calculated from the average ratio of **2**-d_1:**3**-d_1 at 500°. [e] Calculated from the average ratio of 2-d_1:3-d_1 at 550°. [f] Pyrolysis without Vycor chip packing.

Calculations for the primary deuterium isotope effect are set forth. The rate of elimination via path B will be the same for both **1** and **1**-d_2 since deuterium is not involved in

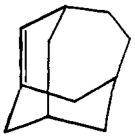
$$\frac{\text{path A}}{\text{path B}} = \frac{2k^A}{k^B}$$

$$\frac{k_H}{k_D} = \frac{k_H{}^A/k_H{}^B}{k_D{}^A/k_D{}^B} \text{ since } k_H{}^B = k_D{}^B$$

the rate-determining step. These values, 2.3 at 500° and 2.3 at 550°, for the primary deuterium isotope effect are very similar to those (1.7-2.4) observed[11] for pyrolyses of other acetates at 500°. This suggests that the carbon-hydrogen bond undergoes scission in the rate-determining step, and that the degree of concertedness is moderate for breaking of the carbon-hydrogen and carbon-oxygen bonds in the present case. The data, again, support the concept of classical ester pyrolysis (Scheme I).

At 550°, the ratio of rates for path A and path B gives a calculated difference in free energy of activation of 1.8 kcal/mol.[21] The conclusion which can be drawn from the labeling experiments is that path A is decidedly favored when the statistical effect is taken into account, indicating that thermodynamic stability of the intermediate bridgehead olefin, **14** or **15**, is the determining factor. The findings at 470° suggest that strain differences between **14** and **15** become more important at the lower temperature (Scheme I).

Although **14** and **15** are both bridged *trans*-cycloheptenes, 3-homoadamantene (**14**) should be appreciably more stable than the 2 isomer **15** because of the additional carbon atom in the bridge. This is substantiated by the results from analogous Hofmann and Cope eliminations[4,5] which gave dimers and Diels-Alder adducts arising almost exclusively from **14**. Apparently, **14** can more closely approach planarity of the double bond at the bridgehead, whereas **15** is somewhat more constrained. Furthermore, the isomeric *trans*-cycloheptene, 1-homoadamantene (**20**), should be more strained than either **14** or **15**. Models of **20** indicate that the double bond cannot approximate a planar geometry as readily as in **14** or **15**.[21] A similar difference has been observed in studies dealing with bicyclo[3.2.2]non-1-ene[6c] (**21**) and bicyclo[3.2.1]oct-1-ene[6d] (**22**), both of which contain a bridged *trans*-cycloheptene. Olefin **21** is generated readily by Hofmann elimination, whereas **22** is formed to only a very minor extent. This difference can be rationalized by the greater constraint placed on the ring system by the methylene bridge as compared with the ethylene branch.



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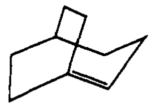

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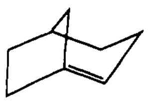

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Because of the strain associated with the distorted alkenes **14** and **15** generated from a tertiary bridgehead position, activation parameters should be somewhat different from those for straightforward *tert*-alkyl acetates. For example, the E_a value would be expected to be higher than that, E_a = 40.0-43.2, calculated for *tert*-butyl acetate.[11]

Experimental Section

Ir spectra were obtained with a Perkin-Elmer 137 spectrophotometer (calibrated with the 1601.8 cm^{-1} band of polystyrene). Varian T-60 and HA-100 instruments were used to obtain NMR data (tetramethylsilane as internal standard). Microanalyses were performed by Baron Consulting Co., Orange, Conn., Microtech, Skokie, Ill., and Dr. R. E. White. Some of the mass spectral data were provided by Dr. Earl Levi. GLC analyses were conducted on a Varian 1800 instrument with a 15% Carbowax 20M on Chromosorb W (45-60 mesh), 10 ft × 0.25 in., copper column. Preparative scale collections were carried out on a Varian 90P instrument, 20% Carbowax 20M on Chromosorb P (30-60 mesh), 20 ft × 0.375 in., copper column. Boiling points (micro) and melting points were obtained with a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Ozone was generated by a Welsbach T-408 ozonizer. The Vycor reactor was heated by a Lindberg heavy-duty furnace with temperature held constant to ±1°.

3-Homoadamantyl Acetate (1).[12] 3-Homoadamantanol[22] (10.0 g, 0.060 mol) was added to sodium acetate (10 g, 0.122 mol) in 125 ml of acetic anhydride. The mixture was refluxed for 4 hr, allowed to cool overnight, and then added to 800 ml of ice-cold 10% H_2SO_4. After being stirred for 15 min, the acid solution was extracted with ether. The organic phase was washed with 5% $NaHCO_3$, then with water, dried, and evaporated to yield 11.8 g of crude product. Vacuum distillation at 82-85° (0.1 mm) gave 10.5 g (84%) of pure product.

Pyrolysis of 1. Compound **1** (2 g) was slowly vaporized during 2-4 hr at 100° and passed through a Vycor tube packed with Vycor chips by means of nitrogen as the carrier gas. The tube was heated at temperatures of 475-600°. Products were collected in three cold traps at Dry Ice-acetone temperature and then were taken up in ether. The ether solution was washed in turn with 5% $NaHCO_3$ and water, then dried and evaporated. A typical run (550°) gave 0.64 g of olefinic material (product recovery was increased by insertion of glass wool in exit tubes). GLC analysis showed the presence of the indicated products. **2** (0.15 g, 11%): bp 190°; *m/e* (rel intensity) 149 (5), 148 (45), 105 (63), 80 (62), and 44 (100); ir (neat) 1625, 995, and 906 cm^{-1}; NMR (CCl_4) δ 4.75-6.27 (typical vinyl pattern, 3 H), 2.25 (s, 3 H), and 1.63 (s, 10 H). **3** (0.29 g, 21%): bp 209°; *m/e* (rel intensity) 149 (11), 148 (100), 133 (16), 91 (46), and 79 (54); ir (neat) 1650, 887, 878, 830, and 807 cm^{-1}; NMR (CCl_4) δ 4.65 (d, J = 7.2 Hz, 2 H), 2.80 (complex t, 2 H), and 2.5-1.4 (m, 12 H). **4**[23] (0.021 g, 1.5%): mp 237-238° (lit.[23a] mp 237-237.5°).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found for **2**: C, 88.87; H, 10.89. Found for **3**: C, 89.05; H, 10.91.

Stabilities of Olefins 2 and 3. The olefin mixtures from decomposition of 3-homoadamantyl acetate were pyrolyzed at 500 and 600° to determine whether either of the alkenes was decomposing appreciably faster than the other. Pyrolysis at 600° of a mixture with a ratio of **3**:**2** of 2.07 gave product in which this ratio changed to 0.388. Thermolysis of olefin mixture, **3**:**2** equaling 2.31, at 500° yielded product with a final ratio of 2.69 for **3**:**2**.

Ozonolysis of 2 and 3. A mixture of **3** (0.448 g, 3.02 mmol) and **2** (0.155 g, 1.05 mmol) was dissolved in 75 ml of CH_2Cl_2 (distilled from CaH_2) and cooled to −50°. Ozonized oxygen (approximately 6 g/hr) was passed into the solution through a sintered glass tube for 20 min. The ozonides were reduced by stirring the solution with 50 ml of 10% HCl and 1 g of Zn metal for 30 min. The organic layer was separated, dried, and evaporated. GLC analysis revealed the presence of 4-protoadamantanone (**5**) (0.26 g, 56%), mp 208-210° (lit.[13b] mp 205-208°), and 3-noradamantanecarboxaldehyde (**6**) (0.064 g, 40%), mp 130-133°: ir (CCl_4) 2670, 1755, and 1195 cm^{-1}; NMR (CCl_4) δ 9.73 (s, 1 H), 2.3-2.7 (m, 3 H), and 1.7-2.1 (m, 10 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found for **6**: C, 79.75; H, 9.10.

4-Hydroxyprotoadamantane[15] (8) and 3-Noradamantylcarbinol[14] (7). Treatment of the carbonyl mixture [**5** (0.75 g, 5.0 mmol) and **6** (0.25 g, 1.69 mmol)] in 100 ml of anhydrous ether with $LiAlH_4$ (1.5 g) at room temperature for 2 hr resulted in conversion to the corresponding alcohols, 4-protoadamantanol (**8**) [exo (24% yield), mp 204-206° (lit.[15] mp 204-206°); endo (41% yield), mp 215-217° (lit.[15] mp 214-216°)] and 3-noradamantylcarbinol (**7**) (28% yield), mp 137-140° (lit.[14] mp 142-144°).

3-Ethylnoradamantane (9) and 4-Methylprotoadamantane (10). A mixture of **3** (0.63 g, 4.25 mmol) and **2** (0.3 g, 2.0 mmol) was hydrogenated for 24 hr at room temperature in 50 ml of absolute ethanol with 0.5 g of 5% palladium on charcoal in a Parr apparatus. After filtration, removal of solvent provided 0.7 g of product. GLC analysis and collection gave: **9** [(0.12 g, 40% yield), bp 195°; ir (neat) 1450, 1360, and 1325 cm^{-1}; NMR (CCl_4) δ 2.10 (m, 3 H), 1.56 (m, 12 H), and 0.90 (t, J = 7 Hz, 3 H)], **10** (endo) [(0.46 g, 73% yield), bp 209°; ir (neat) 1445, 1360 (w), and 1320 (w) cm^{-1}; NMR (CCl_4) δ 4.10 (m, 1 H), 2.2-1.4 (m, 12 H), and 0.95 (d, 3 H)], and **10** (exo) (0.11 g, 17% yield).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found for **9**: C, 87.85; H, 12.14. Found for **10**: C, 87.68; H, 12.29.

1-Methyl-2-adamantyl Formate (11). A mixture of **3** (0.598 g, 4.03 mmol) and **2** (0.265 g, 1.79 mmol) in 5 ml of ether was added to 8 ml of 97% formic acid. After 16 hr at reflux, the reaction mixture was added to ether and 5% $NaHCO_3$. The organic layer was washed with water, dried, and evaporated leaving 1.05 g of crude product. GLC analysis indicated the presence of **2** (0.18 g, 68% recovery) and **11** (0.73 g, 93% yield): bp 253°; ir (neat) 1700, 1440, 1170, 962, and 940 cm^{-1}; NMR (CCl_4) δ 8.13 (s, 1 H), 4.93 (m, 1 H), 2.1-1.6 (m, 13 H), and 0.80 (s, 3 H).

Anal. Calcd for $C_{12}H_{18}O$: C, 74.19; H, 9.34. Found for **11**: C, 73.96; H, 9.42.

1-Methyladamantan-2-ol[16a] (12). Compound **11** (0.2 g) was heated at reflux in 25 ml of 25% NaOH with subsequent steam distillation for 45 min. The distillate was extracted with ether and dried. Evaporation of solvent provided **12**, mp 168-170° (lit.[16a] mp 168.5-170°).

1-Methyladamantan-2-ol (12). The olefin mixture [**2** (0.242 g, 1.63 mmol) and **3** (0.626 g, 4.22 mmol)] was added to 50 ml of 50% H_2SO_4 and stirred at 35° for 6 hr. GLC analysis indicated essentially complete conversion of **3** to **12**. Alkene **2** was unchanged (80% recovery) with no product detected with the proper retention time for 2-methyladamantan-1-ol.

Polymerization of 3. Pure **3** (0.174 g, 1.17 mmol) was dissolved in 2 ml of dry CH_2Cl_2 and cooled to −75°. Gaseous BF_3 was introduced above the solution at this temperature for 1 hr and at room temperature for 2 hr. The polymer was precipitated by pouring into 7 ml of methanol. The crude yield of **13** was 0.161 g (93%). Reprecipitation from 2 ml of CH_2Cl_2 with 5 ml of methanol gave 0.0311 g of white solid: mp 133-142°; ir (CCl_4) 1528, 1433, 1240, and 997 cm^{-1}; NMR (CCl_4) δ 2.1-1.4 (m with peaks at 1.95, 1.91, 1.71, and 1.54).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found for **13**: C, 89.06; H, 10.75.

3 from 5 by the Wittig Reaction. Phenyllithium (12.7 mmol) was added slowly to methyltriphenylphosphonium bromide (2.9 g, 8.12 mmol) in 25 ml of ether under a nitrogen atmosphere. After 4 hr of stirring at room temperature, the ketone **5** (0.18 g, 1.1 mmol) in ether (10 ml) was added, and the mixture was refluxed for 24 hr. Ether was added after cooling and the precipitate was filtered. The ether layer was washed with water, dried, and evaporated to approximately 1 ml. GLC analysis indicated a 10% yield of 4-methyleneprotoadamantane (**3**).

3-Homoadamantyl-*4,4-d*$_2$ Acetate (1-*d*$_2$). The deuterated acetate was made in 86% yield from deuterated 3-homoadamantanol (see preparation of **1**) which was obtained by the method of Stetter and Goebel[22] (replacement of $LiAlH_4$ by $LiAlD_4$).

Pyrolysis of 1-*d*$_2$.[24] Compound **1**-d_2 (2.5 g, 0.012 mol) was pyrolyzed at 550° as described in a previous section to give 0.86 g of product. GLC and NMR analysis indicated **3**-d_1 (0.12 g, 6.8% yield), **3**-d_2 (0.44 g, 25% yield) [NMR (**3**-d_1 and **3**-d_2) ($CDCl_3$) δ 4.67 (d, J = 7.2 Hz, 0.5 H), 2.54-1.3 (m, 11.75 H)], **2**-d_1 (0.14 g, 7.8% yield) [NMR ($CDCl_3$) δ 4.92 (ill-resolved d, 2 H), 2.23 (s, 3 H), and 1.63 (s, 10 H)], and **4**-d_1 (0.018 g, 1% yield). Mass spectral analysis of **3**-d_1 and **3**-d_2 gave *m/e* (parent ions) 150 (76%) and 149 (24%) rel intensities.

Pyrolysis of 1-Adamantylcarbinyl Acetate (18). Decomposition of 2.0 g of **18** at 550° gave 0.86 g of material which was 97% starting acetate. The remaining 3% was mostly olefins **2** and **3**, relative amounts of 26 and 74%, respectively (**3**:**2** = 2.85).

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(24) A minor amount of absorption was present in the region of the lower field hydrogen for 2-d_1, possibly derived from some 4-H present in the deuterated acetate. On the other hand, there was no evidence of the triplet associated with $=CH_2$ when the lower field hydrogen is present. 1-AdCD_2NH_2 was essentially 100% deuterated according to NMR. It was difficult to ascertain the purity, in relation to deuterium content, of the derived acetate partly because of the instability of the molecular ion in mass spectral analysis. A minor amount of 4-H may be present (possible exchange during diazotization). The presence of nondeuterated ester would increase the rate of elimination via path A, thus giving an increase in the value for path A/path B. Similarly, there would be a decrease in the value for the primary deuterium isotope effect.

Photochemical Rearrangements of Indazoles. Investigation of the Triplet Excited States of 1- and 2-Methylindazole[1]

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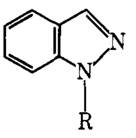
Abstract: The triplet states of 1-methylindazole (1-MI) and 2-methylindazole (2-MI) were studied by flash absorption and flash emission spectroscopy at room temperature and by emission spectroscopy and ESR spectroscopy at liquid-nitrogen temperatures. The triplet states exhibit similar absorption spectra with maxima at 420 and 405 nm, respectively. Comparable first-order rate constants of approximately 10^4 sec^{-1} for decay of the triplets of 1-MI and 2-MI were obtained by flash absorption and flash emission. Revised values of the triplet energies of 66.7 and 67.3 kcal were obtained for 1-MI and 2-MI, respectively. The triplets were quenched with oxygen and with piperylene. The photochemical rearrangements of 1-MI to *N*-methylanthranilonitrile and 2-MI to 1-methylbenzimidazole must proceed from the singlet excited states since they are not quenched by oxygen or dienes. High concentrations (10^{-1} *M*) of dienes react with the singlet state of 1-MI. Triplet energy transfer to cyclohexadiene (10^{-2} to 10^{-3} *M*), under conditions where no inhibition of product formations was observed, was established by the isolation of cyclohexadiene dimers. Radicals were detected by ESR spectra on irradiation of 1-MI and 2-MI. These may be formed by the cleavage of the N–N bonds in these compounds.

Detailed analyses have been carried out on the products of the photoisomerization of indazole and substituted indazoles.[2,3,4] Photolysis of the *N*(1)-alkylated indazoles (**1**) gives the corresponding alkylaminobenzonitriles (**4**) in 10–60% yield, while photolysis of *N*(2)-alkylated indazoles (**2**) proceeds rapidly and in high yield (~85%) to the *N*(1)-alkylated benzimidazoles (**3**). Indazoles without *N*-alkyl groups (**1**, R = H) give both benzimidazoles (**3**, R = H) and aminobenzonitriles (**4**, R = H) on irradiation.



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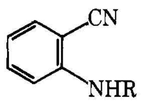

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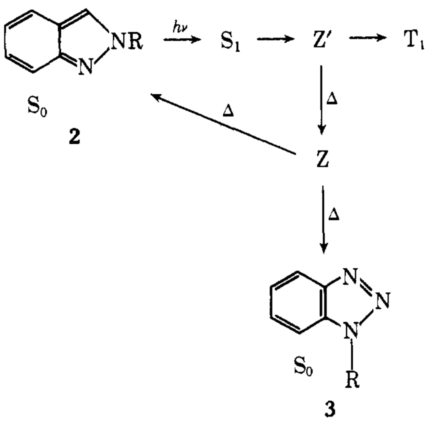
The photoisomerization of *N*(2)-alkylindazoles (**2**) is intramolecular and proceeds from the singlet excited state.[3] An intermediate having a lifetime of several seconds was detected by uv spectra. In addition, the decrease in the quantum yield of the photoisomerization with pH suggested the presence of an intermediate, the protonated form of which does not yield the benzimidazole product.[3] The yield of this intermediate (Z, Scheme I) was found to be independent of exciting wavelength and dependent on the temperature. This temperature dependence requires the presence of a second intermediate (Z′, Scheme I) which is stable at low temperatures. Labhart et al.[3] proposed the mechanistic pathway in Scheme I, the photoisomerization of 2-alkylindazoles (**2**) to 1-alkylbenzimidazoles (**3**). The exact nature of the two proposed intermediates Z and Z′ is not known.

The present work was carried out to obtain more information about the intermediate(s) involved in the photoisomerization of 1-MI and 2-MI and the multiplicity of the excited state from which they are derived.

Scheme I



Experimental Section

Spectroquality solvents supplied by Matheson Coleman and Bell were used without further purification. Indazole was obtained from Aldrich Chemical Co. and was purified by vacuum sublimation (mp 147.5–148.5°). 1-MI and 2-MI were prepared by the methylation of indazole.[5] Twice-sublimed 1-MI (mp 60–61°) and twice-recrystallized 2-MI (mp 54.5–56.0°) were used in these studies. Degassing was done by three or four freeze-pump-thaw cycles. Uv spectra were run on a Unicam SP 800A spectrophotometer. A low-temperature cell developed by Richtol and Klappmeier[6] was used to measure the absorption spectra at low temperatures. The NMR spectra were recorded on a Varian T-60 spectrometer using Me_4Si as standard.

Flash Photolysis. Kinetics of transient(s) decay and transient absorption spectra were measured using the flash-photolysis apparatus described elsewhere.[7] Light from the flash lamp was filtered through CCl_4, and light from the continuous analyzing beam was filtered through plate glass. The rate constants for transient decay at room temperature were measured by flash-emission techniques using an FP-2R flash photolysis apparatus (Northern Precision

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