Generation and Reactions of 2-(1-Adamantyl)adamantene. Rearrangement to 3-(1-Adamantyl)-4-protoadamantylidene

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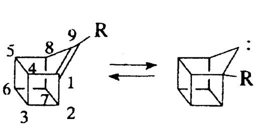
The S_N1 methanolysis of (1-adamantyl)(3-noradamantyl)methyl heptafluorobutyrate at 100 °C yielded (1-adamantyl)-(3-noradamantyl)methyl methyl ether (**17**), 2-(1-adamantyl)-1-methoxyadamantane (**18**), and 4-(1-adamantyl)-3-methoxyprotoadamantane (**19**) in a 2 : 65 : 33 ratio. The methanolysis of (1-adamantyl)(3-noradamantyl)diazomethane (**7**) at 0 °C also yielded **17**, **18**, and **19** in a 4 : 33 : 63 ratio. On the other hand, the photolysis of **7** in 99 : 1 (v/v) hexane–methanol gave **17**, **18**, 2-(1-adamantyl)-2-methoxyadamantane (**25**), and 2-(1-adamantyl)-2,4-didehydroadamantane (**20**) in a 30 : 9 : 36 : 25 ratio. Presence of triethylamine decreased the yields of ethers **17**, **18**, and **25**, and increased the yield of **20** to 46%. The formation of a considerable amount of **17** and the absence of **19** in the photolysis products indicate the generation of (1-adamantyl)(3-noradamantyl)methylidene (**8**). The formation of **25** and **20** suggests that the generated carbene **8** rearranges to 2-(1-adamantyl)adamantene (**3b**) and then gives 3-(1-adamantyl)-4-protoadamantylildene by the subsequent retro-insertion. An attempt to isolate **3b** in the photolysis of **7** in cyclohexane failed, and the sole isolated product was **20**.

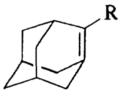
For the past decade, the chemistry of anti-Bredt olefins has again been a field of great interest for organic chemists.[1] This can probably be ascribed to rapid progress in cubene[2] and homocubene[3,4] chemistry. Bridgehead olefins are usually generated by three methods: Dehalogenation of 1,2-dihalides, Hofmann elimination, and carbene rearrangement. Rearrangements of carbenes to olefins are usually exothermic and irreversible reactions, but a few highly strained bridgehead olefins were found to undergo the reversion to carbenes. Eaton et al.[4] showed that 9-phenyl-1(9)-homocubene (**1b**) rearranges to 1-phenyl-9-homocubylidene (**2b**) (Scheme 1). Subsequently, Jones et al. found that parent 1(9)-homocubene (**1a**) can also rearrange to 9-homocubylidene (**2a**) and that the equilibrium constant for this reaction was estimated to be approximately unity at room temperature; they performed trapping experiments.[3c,3d,3f,3g]

Adamantene (**3a**) is one of the most strained olefins; its synthesis has been extensively studied for a long time (Scheme 2).[5—8] Recently, Jones et al. studied the generation and reaction of adamantene (**3a**) in the gas phase by the ring expansion of (3-noradamantyl)carbene (**4**). They found that **3a** can rearrange to 4-protoadamantylidene (**5**) by the retro-insertion into carbon–carbon bond, leading to 4-protoadamantene (**6**) (Scheme 3).[6a] However, in solution, **3a** gives [2+2] dimers almost quantitatively;[7,8] no evidence of olefin–carbene rearrangement has been obtained in solution. This might be because the rearrangement process would be slower than dimerization of **3a**.



1a (R = H) **2a** (R = H)
1b (R = Ph) **2b** (R = Ph)

Scheme 1.

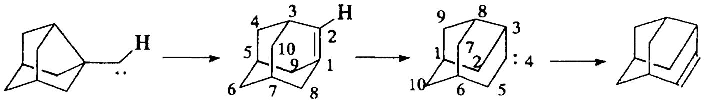


3a (R = H)
3b (R = 1-Ad)

Scheme 2.

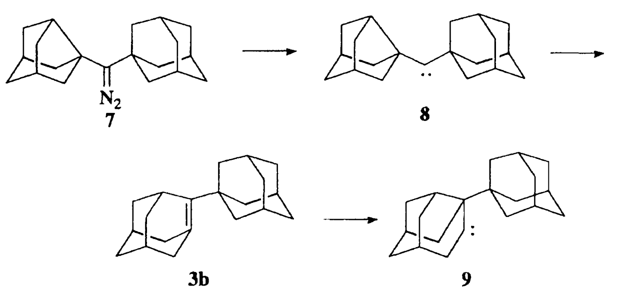
The replacement of the vinyl hydrogen in trisubstituted bridgehead olefins with a bulky group such as the 1-adamantyl group has been suggested to inhibit dimerization and markedly enhance kinetic stability.[9] We expected that the dimerization and other intermolecular reactions of 2-(1-adamantyl)adamantene (**3b**) in solution would be suppressed due to the protection by the adamantyl substituent, and wished to create the possibility of investigation of its reaction behavior and the olefin–carbene rearrangement to give 3-(1-adamantyl)-4-protoadamantylidene (**9**) (Scheme 4).

We here report the generation and reaction of 2-(1-adamantyl)adamantene (**3b**) which is generated by a carbene route. Since carbenes and the precursor diazomethanes are generally protonated in methanol and further react to give cationic products, we also investigated the solvolysis of (1-adamantyl)(3-noradamantyl)methyl heptafluorobutyrate (**10**), which would undoubtedly react through a cationic intermediate (Scheme 5). We compared the product distribution

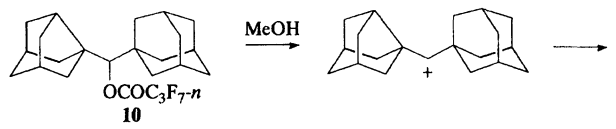


4 **3a** **5** **6**

Scheme 3.



Scheme 4.



Scheme 5.

in the photolysis of (1-adamantyl)(3-noradamantyl)diazomethane (**7**) with that in solvolysis of **10**. These results were explained by the intervention of the olefin–carbene rearrangement.

Results and Discussion

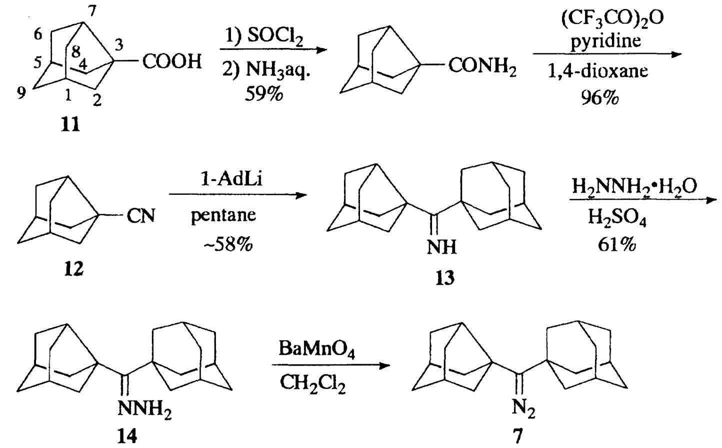
Synthesis. The synthesis of (1-adamantyl)(3-noradamantyl)diazomethane (**7**) is shown in Scheme 6. 3-Noradamantanecarboxylic acid (**11**) was converted to 3-noradamantanecarbonitrile (**12**) by amidation and subsequent dehydration. The reaction of **12** with 1-adamantyllithium[10] in pentane at −78 °C yielded (1-adamantyl)(3-noradamantyl)methanimine (**13**). The crude imine **13** was converted to the corresponding hydrazone **14** by heating with hydrazine monohydrate. Diazomethane **7** was synthesized by the $BaMnO_4$ oxidation of **14**; it was used for the generation of olefin **3b** without further purification. The purity of **7** was estimated to be 90—95% by NMR.

(1-Adamantyl)(3-noradamantyl)methanol (**15**) was synthesized by the reaction of 3-noradamantanecarbaldehyde with 1-adamantylmagnesium bromide[11] in ether (Scheme 7). Since the tosylate and mesylate were too unstable to be isolated, **15** was converted to the corresponding heptafluorobutyrate **10**.

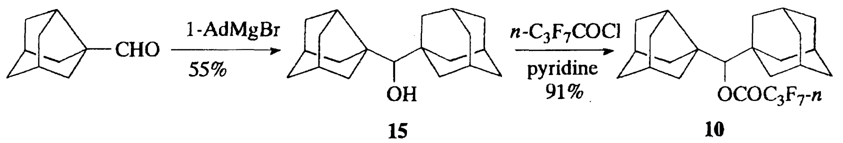
1-Adamantyl 3-noradamantyl ketone, which was prepared by the pyridinium chlorochromate oxidation of **15**, could not be converted to **14**.

Solvolysis of (1-Adamantyl)(3-noradamantyl)methyl Heptafluorobutyrate (10) through Cationic Intermediate. The rates of the solvolysis of heptafluorobutyrate **10** were titrimetrically determined in MeOH at 75 and 100 °C in the presence of 2,6-lutidine. Good first order behavior ($r > 0.9999$) was observed over 60% reaction. Then the reaction began to deviate from the first-order behavior, probably because of esterification of heptafluorobutyric acid with methanol. The rate constants and activation parameters are summarized in Table 1.

Shiner, Jr., and Stoelting[12] studied the solvolysis of 1-sub-



Scheme 6.



Scheme 7.

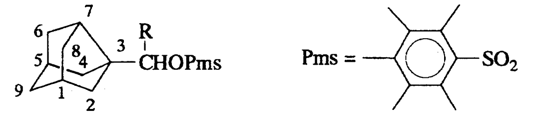
Table 1. Rate Constants for the Methanolysis of (1-Adamantyl)(3-noradamantyl)methyl Heptafluorobutyrate (**10**)[a]

Temp °C	k s^{-1}	$\Delta H^{\ddagger}$ $kJ\,mol^{-1}$	$\Delta S^{\ddagger}$ $J\,mol^{-1}\,K^{-1}$
100.0	$2.76(\pm 0.04)\times 10^{-5}$ [b]		
75.0	$1.44(\pm 0.02)\times 10^{-6}$ [b]		
25.0	8.82×10^{-10} [c]	125	2

a) Buffered with 0.025 mol dm^{-3} 2,6-lutidine. b) Titrimetrically determined. c) Calculated from data at other temperatures.

stituted (3-noradamantyl)methyl pentamethylbenzenesulfonates (**16**). They reported that the solvolysis of (3-noradamantyl)methyl ester (**16**: R = H) is accelerated by a factor of 10000 owing to C(3)–C(7) σ-participation, and also that the increase in the bulkiness of the α-substituent (R) reduces this acceleration by a factor of up to 100 (R = *t*-Bu) (Scheme 8). They suggested that this is because the substituent R reduces the participation by interfering with the approach of C(7) to C^+, reducing C^+–C(7) σ-bonding in the transition state of the ionization and the anchimeric acceleration. Therefore, the σ-participation in the 3-noradamantyl group in the solvolysis of (1-adamantyl)(3-noradamantyl)methyl heptafluorobutyrate (**10**) was expected to be very weak.

For the product study, the solvolysis of heptafluorobutyrate **10** was carried out in MeOH at 100 °C for 10 half-lives. Gas chromatography (GC) analysis of the products was not successful owing to the low vapor pressure of the methyl ethers. After aqueous work-up, the resulting oil was analyzed by ^1H NMR (400 MHz) to determine the yields of products. The products were (1-adamantyl)(3-noradamantyl)methyl methyl ether (**17**), 2-(1-adamantyl)-1-methoxyadamantane (**18**), and 4-(1-adamantyl)-3-methoxyprotoadamantane (**19**) in a 2 : 65 : 33 ratio (Scheme 9). The NMR spectra of **17** and **18** were identical with those of the authentic samples synthesized by the methylation of the corresponding alcohols. 2-(1-Adamantyl)-1-adamantanol, the precursor of the authentic sample **18**, was prepared by the formolysis of (1-adamantyl)(3-noradamantyl)methanol (**15**). The identification of **19** rested on ^{13}C NMR spectra, which were similar to those of 4-*t*-butyl-3-methoxyprotoadamantane reported in the literature.[12b)] The stereochemistry of the adamantyl group in **19** could not undoubtedly be determined, but Shiner, Jr., and Stoelting[12b)] concluded that the solvolysis of **16** (R = *i*-Pr, *t*-Bu) gives more *endo*-4-R-3-protoadamantyl ether than the *exo* isomer, since the energy of transition state for the formation of the *exo*-4-R-3-protoadamantyl cation from **16** was calculated to be higher than that of the *endo*-4-R-3-protoadamantyl cation by MMX. Therefore **19** is also expected to have an *endo* configuration.



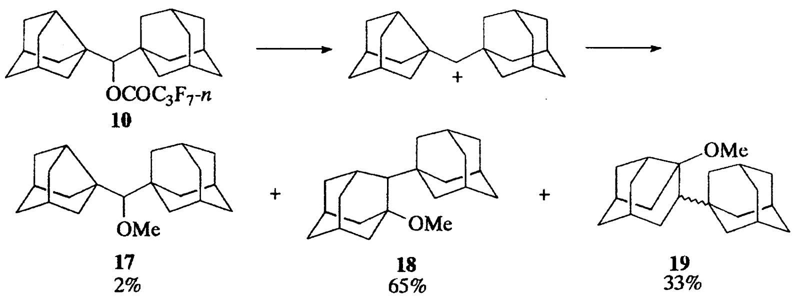
16

Scheme 8.

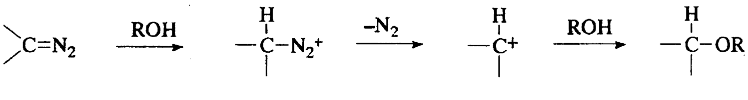
Shiner, Jr., and Stoelting[12)] found that **16** with R = Me rearranged to give only the 2-methyl-1-adamantyl cation, but that **16** with R = Et, *i*-Pr, *t*-Bu yielded the corresponding 3-protoadamantyl cations as well, and that their amount increased with the bulkiness of the substituent. The solvolysis of **10** yielded 33% of 3-protoadamantyl ether **19**, supporting the conclusion[12b)] that the bulky α-substituent reduces the C(3)–C(7) σ-participation of noradamantyl group by congestion in the transition state.

No homoadamantyl compounds were formed from **10** by ring expansion of C–C bond in the adamantyl group, indicating that the σ-participation of the adamantyl group would not be effective. The product distribution **17** : **18** : **19** = 2 : 65 : 33 suggests that the (1-adamantyl)(3-noradamantyl)methyl cation immediately rearranges to adamantyl and protoadamantyl cations.

Methanolysis of (1-Adamantyl)(3-noradamantyl)diazomethane (7). The photolysis of diazoalkanes in alcohols is usually accompanied by an undesired reaction.[13)] The majority of a diazoalkane is protonated even by weakly acidic alcohols to give the corresponding alkanediazonium ion and

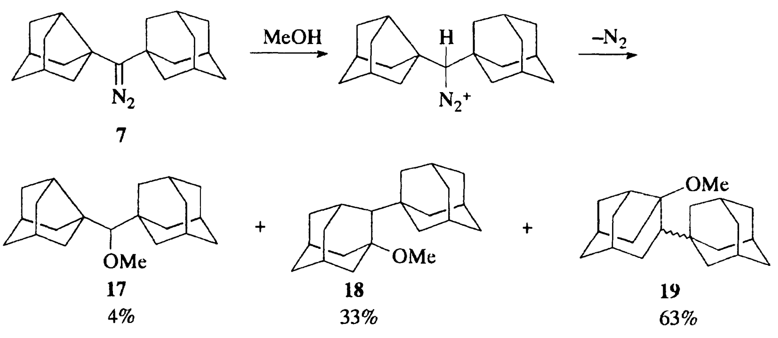


Scheme 9.

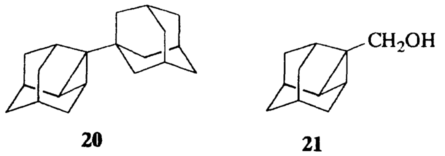


$$\rangle C{=}N_2 \xrightarrow{ROH} -\overset{H}{\underset{|}{\overset{|}{C}}}-N_2^+ \xrightarrow{-N_2} -\overset{H}{\underset{|}{\overset{|}{C}}}+ \xrightarrow{ROH} -\overset{H}{\underset{|}{\overset{|}{C}}}-OR$$

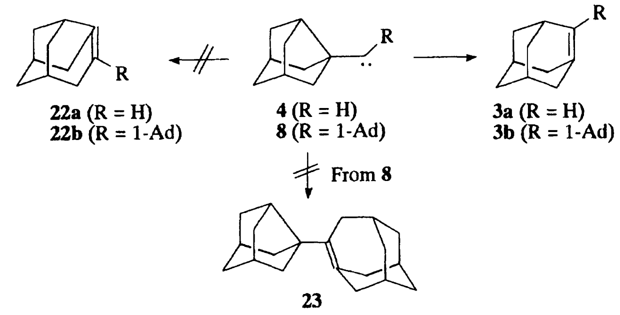
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

yields products (Scheme 10). A carbocation which is yielded by the decomposition of alkanediazonium ion is called "hot", "high energy", or "poorly solvated" cation and is *different* from the "normal" cation formed during the solvolysis of an ester; the carbocation which is formed as a solvolysis intermediate has been called "cold".[13] They are quite distinct in behavior, having different product distributions and, often, different products.[13,14]

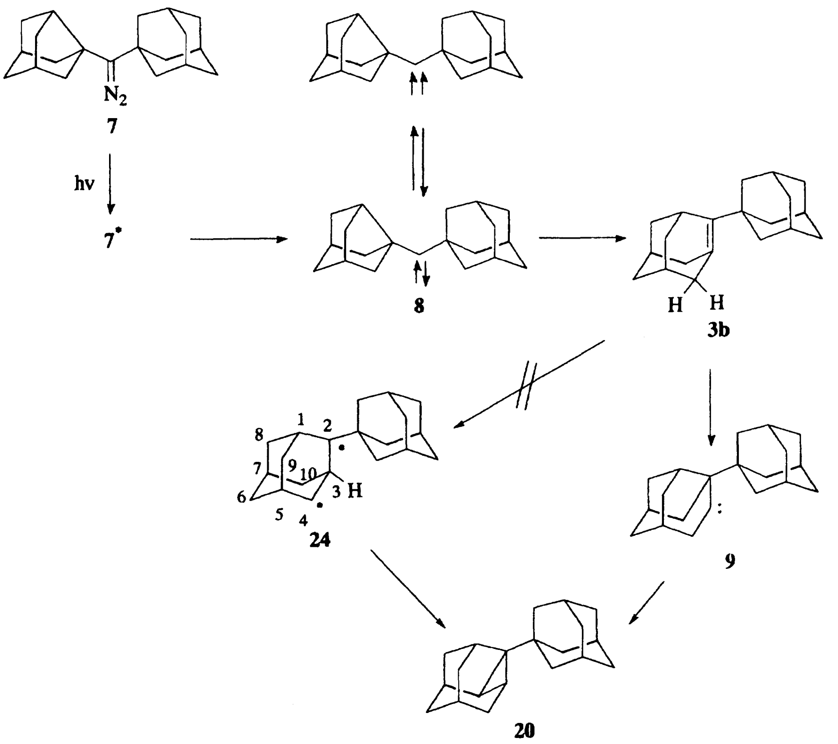
When a suspension of diazomethane **7** in methanol was stirred in the dark at 0 °C, it was gradually decolorized and, after 12 h, it became colorless. After removal of the solvent, NMR analysis showed that the products were composed of three ethers **17**, **18**, and **19** in a ratio of 4 : 33 : 63 (Scheme 11). The fraction of the ring expansion toward protoadamantyl skeleton was much larger than that in solvolysis of **10**. The different product distributions would be due to the difference in the behavior of hot and cold cations.

Photolysis of (1-Adamantyl)(3-noradamantyl)diazomethane (7) in Hexane and Cyclohexane. When diazomethane **7** was photolyzed in a hexane solution at 0 °C, ca. 20% of 2-(1-adamantyl)-2,4-didehydroadamantane (**20**) was formed. It was separated by high performance liquid chromatography (HPLC) and identified by the comparison of the NMR spectra with those of 2,4-didehydro-2-(hydroxymethyl)adamantane (**21**) (Scheme 12).[15] The other products were unknown hydrocarbons, which might have been formed by insertion of generated carbene **8** into C–H bonds of hexane or other molecules. The photolysis of **7** in cyclohexane at 14 °C gave mainly **20** in a yield of 35% as well as unreacted **7**. There are three possible ways for the rearrangement of carbene **8**: The ring expansion of the shorter and longer bridges of the noradamantyl framework to give **3b** and 4-(1-adamantyl)-3-protoadamantene (**22b**), respectively, and

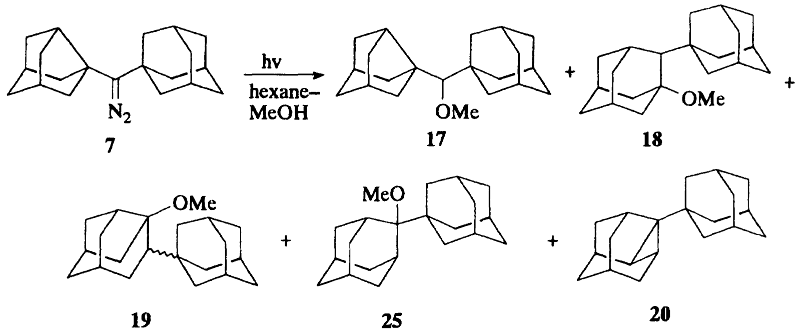
Table 2. Heats of Formation (ΔH_f °), Strain Energies (*SE*), and Olefinic Strain Energies (*OS*) of 2-R-Adamantene [**3a** (R = H), **3b** (R = 1-Ad)], 4-R-3-Protoadamantene [**22a** (R = H), **22b** (R = 1-Ad)], and 4-(3-Noradamantyl)-3-homoadamantene (**23**) Calculated by MM2(87) and MM3(92) (kJ mol^{-1})[a]

	MM2(87)			MM3(92)		
Compound	ΔH_f°	*SE*	*OS*[b]	ΔH_f°	*SE*	*OS*[b]
Adamantane	−132.0	43.6		−133.9	29.3	
Adamantene (**3a**)	91.5	157.9	114.2	98.4	148.4	119.1
Protoadamantane	−86.7	88.9		−82.5	80.8	
3-Protoadamantene (**22a**)	123.3	189.5	100.6	118.6	168.5	87.7
2-(1-Adamantyl)adamantane	−239.9	130.4		−198.6	111.6	
2-(1-Adamantyl)adamantene (**3b**)	−12.7	223.4	93.0	−5.9	192.5	81.0
4-(1-Adamantyl)protoadamantane	−181.3	156.5		−170.6	139.6	
4-(1-Adamantyl)-3-protoadamantene (**22b**)	6.1	249.7	93.2	13.7	204.5	64.9
4-(3-Noradamantyl)homoadamantane	−145.1	192.6		−123.0	187.2	
4-(3-Noradamantyl)-3-homoadamantene (**23**)	36.1	272.2	79.6	49.5	248.4	61.2

a) Calculations refer to the most stable geometry of each compound; where necessary, various conformations were tested.
b) Difference in strain energies of alkene and the corresponding alkane. These often do not correspond to the same conformation.



Scheme 14.



Scheme 15.

the expansion of the adamantyl framework to give 4-(3-noradamantyl)-3-homoadamantene (**23**) (Scheme 13). However, the ring expansion in (3-noradamantyl)methylidene (**4**) and (1-norbornyl)methylidene has been shown by Jones et al.[6a)] to take place only through the shorter bridge.

The heats of formation, strain energies, and olefinic strain (OS) values[16)] of adamantene (**3a**) and 3-protoadamantene (**22a**) were calculated with Allinger's MM2[17)] and MM3[18)] methods. The results are summarized in Table 2. The strain energy of a bridgehead olefin is a composite of the extra strain associated with the double bond and the residual strain of the carbon skeleton.[16)] The latter can be approximated by the strain energy of the parent hydrocarbon. The OS value of **3a** was calculated to be larger than that of **22a** by 13.6 kJ mol^{-1} by MM2 and 31.4 kJ mol^{-1} by MM3, but the strain energy of **3a** is smaller than that of **22a** by 31. 6 kJ mol^{-1} by MM2 and by 20.1 kJ mol^{-1} by MM3. These calculations show that the double bond in **3a** is more strained than in **22a**, but **3a** is more stable than **22a** as a whole molecule. 2-(1-Adamantyl)-adamantene (**3b**) was also calculated to be more stable than 4-(1-adamantyl)-3-protoadamantene (**22b**) by 26.3 kJ mol^{-1} by MM2 and by 12.0 kJ mol^{-1} by MM3 and more stable than 4-(3-noradamantyl)-3-homoadamantene (**23**) by 48.8 kJ mol^{-1} by MM2 and by 55.9 kJ mol^{-1} by MM3 (Table 2). These results support the specific ring expansion of the shorter C(3)– C(7) bond of the noradamantyl framework in (3-noradamantyl)carbenes **4** and **8** to adamantenes **3a** and **3b**, respectively.[6a)]

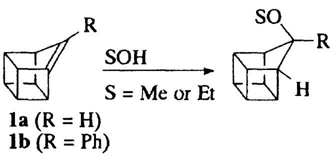
A probable mechanism for the formation of **20** is shown in Scheme 14. Carbene **8**, which is generated from diazomethane **7**, rearranges to 2-(1-adamantyl)adamantene (**3b**).[19,20)] Its subsequent retro-insertion gives 3-(1-adamantyl)-4-protoadamantylidene (**9**),[21)] and affords **20** by intramolecular γ-insertion in **9**. The isomerization of **3b** to adamantane-2,4-diyl biradical (**24**) via the hydrogen shift would be excluded because of unfavorable orbital overlapping.[22)]

Photolysis of (1-Adamantyl)(3-noradamantyl)diazomethane (7) in Hexane in the Presence of Methanol. A solution of diazomethane **7** was photolyzed in a mixture of hexane–methanol [95 : 5 or 99 : 1 (v/v)] at 0 °C. After

Table 3. Yields (%) of the Products of the Photolysis of (1-Adamantyl)(3-noradamantyl)diazomethane (**7**) (0.1 mol dm^{-3}) in Hexane–MeOH (v/v) at 0 °C

Hexane : MeOH (v/v)	**17**	**18**	**19**	**25**	**20**
95 : 5[a)]	30	28	10	21	11
99 : 1[a)]	30	9	<1	36	25
99 : 1[b)]	22	3	<1	29	46

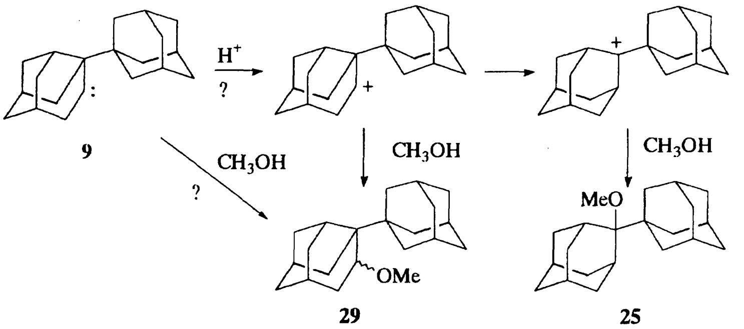
a) In the absence of base. b) In the presence of triethylamine (0.2 mol dm^{-3}).



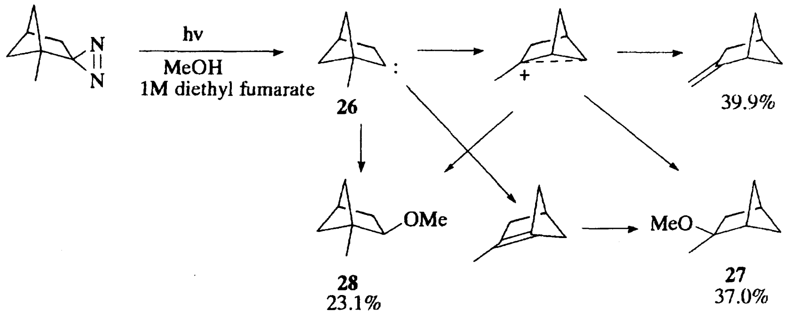
1a (R = H)
1b (R = Ph)

Scheme 16.

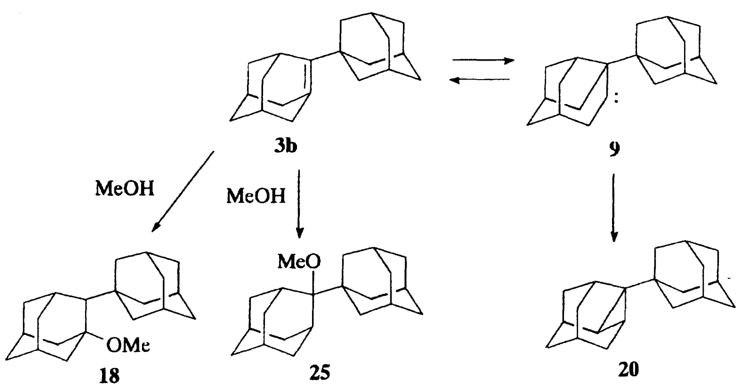
evaporation of the solvent, the product distributions were determined by NMR analysis. The results are summarized in Table 3. The products of the photolysis in 95 : 5 (v/v) hexane–methanol were **17**, **18**, **19**, 2-(1-adamantyl)-2-methoxyadamantane (**25**), and **20** in a ratio of 30 : 28 : 10 : 21 : 11 (Scheme 15). Ether **25** was identified by the comparison of its spectroscopic data with those of the authentic sample that was prepared by the methylation of the corresponding alcohol.[23)] A part of **17**, **18**, and **19** would be formed via carbocationic intermediates generated by the reaction of **7**, excited **7** (**7***),[24)] and/or carbene **8** with methanol. When the protonation of **7** is postulated to occur, the products should be composed of **17**, **18**, and **19** in the ratio of 4 : 33 : 63 (see above). The formation of 10% of **19** indicates that, if any, at most 16% (= 10/0.63) of diazomethane **7** might have decomposed by the protonation with methanol, and that the rest of **7** yielded carbene **8**. The formation of **20** suggested the formation of 2-(1-adamantyl)adamantene (**3b**) and its rear-



Scheme 17.



Scheme 18.



Scheme 19.

rangement to 3-(1-adamantyl)-4-protoadamantylidene (**9**).

When the methanol content in the solvent was decreased from 5 to 1 vol%, the photolysis of diazomethane **7** gave **17**, **18**, **19**, **25**, and **20** in a ratio of 30 : 9 : < 1 : 36 : 25 (Table 3). The yields of **18** and **19** decreased and the yields of **20** and **25** increased. The absence of **19** suggests no occurrence of the protonation of diazomethane **7**, **7***, and carbene **8**. The photolysis in hexane–MeOH (99 : 1 v/v) containing 0.2 mol dm^{-3} triethylamine also yielded **17**, **18**, **19**, **25**, and **20** in a ratio of 22 : 3 : < 1 : 29 : 46. The yield of **20** which was formed via the olefin-carbene rearrangement increased, most probably because the base decreased the ability of MeOH toward addition to **8** and **3b** by lowering the acidity of the medium.

The formation of **25** can be explained by either of the following two mechanisms: (i) The double bond of 2-adamantyladamantene (**3b**) has the contribution of a zwitterionic nature and the addition of MeOH gave 2-methoxyadamantane **25**. A similar mechanism has been suggested to explain the reaction of 9-phenyl-1(9)-homocubene (**1b**)[4)] with EtOH (Scheme 16). Jones, Jr. et al.[3c)] also found that the regiospecific addition of methanol to 1(9)-homocubene (**1a**) gave 9-methoxyhomocubane. (ii) The generated **3b** rearranges to 4-protoadamantylidene **9**, and gives the 4-protoadamantyl cation by subsequent protonation. The secondary cation rearranges quickly to the tertiary 2-adamantyl cation and is trapped with methanol to give **25** (Scheme 17).

Kirmse et al.[25)] found that the reaction of 1-methylbicyclo[2.1.1]hex-2-ylidene (**26**) with methanol gave 37% of 2-methoxy-2-methylbicyclo[2.1.1]hexane (**27**) as well as 23% of 2-methoxy-1-methylbicyclo[2.1.1]hexane (**28**). They suggested that **27** was formed through the cationic intermediate (Scheme 18). The formation of a considerable amount of **28** led us to expect that, if carbene **9** reacted with methanol, it would have given 3-(1-adamantyl)-4-methoxyprotoadamantane (**29**) to some extent as well as **25** (Scheme 17). However, no other ethers than **17**, **18**, **19**, and **25** were obtained from **7**. This result suggests that most, or all, of **25** was formed by the methanol addition to olefin **3b** (Scheme 19). No occurence of the cationic reaction of **7**, **7***, and **8** in 99 : 1 (v/v) hexane–MeOH (see above) suggests that the methanol addition to olefin **3b** also gives **18**. The regioselectivity of this methanol addition would be controlled by the stability of the cations yielded by the protonation of **3b**.

No formation of **29** may be interpreted by assuming the fast intramolecular γ-insertion of carbene **9** to give **20**.[25b)] (1-Adamantyl)(3-noradamantyl)methylidene (**8**) rearranged to 2-(1-adamantyl)adamantene (**3b**) by 1,2-carbon migration as well as giving (1-adamantyl)(3-noradamantyl)methyl methyl ether (**17**) by the reaction with methanol, whereas 3-(1-adamantyl)-4-protoadamantylidene (**9**) gave only 2-(1-adamantyl)-2,4-didehydroadamantane (**20**) by intramolecular 1,3-hydrogen migration. Heats of formation for **3b**, **20**, (1-adamantyl)(3-noradamantyl)methane, and 3-(1-adamantyl)-protoadamantane are calculated to be −12.7, −77.6, −186.4, and −174.9 kJ mol^{-1}, respectively, by MM2. In the first approximation we assume that the difference between the heats of formation of carbenes and the corresponding hydrocarbons is constant, $-\Delta$. It follows that the heat of reaction from **3b** to **8** is $-\Delta+173.7$ kJ mol^{-1} and that from **9** to **20** is $-\Delta+97.3$ kJ mol^{-1}. This suggests that the 1,3-hydrogen migration in **9** is much more exothermic and presumably faster than the 1,2-carbon migration in **8** and methanol addition to **9**.

Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin–Elmer 1640 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL EX400 (400 MHz) or JEOL GSX270 (270 MHz) spectrometer. In all NMR measurements, TMS was used as an internal standard. ^{13}C NMR spectra were obtained with a JEOL EX400 (100 MHz) or JEOL GSX270 (67.8 MHz) spectrometer; chemical shifts were measured relative to $CDCl_3$ and expressed with reference to TMS. Quantitative elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. High-resolution mass analyses were performed with a JEOL JMS-HX110 mass spectrometer using electron impact ionization. Absolute methanol was distilled from sodium methoxide. All the anhydrous solvents used for synthetic work were purified by standard procedures. Other commercially available reagents were of reagent-grade quality and used as received. Medium pressure liquid chromatography (MPLC) was conducted on Merck silica gel 60 (230—400 mesh). All photoreactions were conducted in quartz tubes, using a 100-W high-pressure Daiko HB-100 mercury vapor lamp. The concentration of alkyllithium was determined by titration with 1-pyreneacetic acid[26)] or *N*-pivaloyl-*o*-toluidine.[27)] 2-(1-Adamantyl)-2-adamantanol[23)] was synthesized following a literature procedure.

3- Noradamantanecarboxamide. A mixture of 3-noradamantanecarboxylic acid (**11**) (4.01 g, 24.1 mmol) and thionyl chloride (4.22 ml, 57.9 mmol) was refluxed for 1.5 h and then cooled to ambient temperature. Ether was added and a 28% ammonia solution (50 ml) was added at 0 °C. Stirring was continued for a further 2 h at room temperature, and then the mixture was extracted with CH_2Cl_2 (5×20 ml). The combined extracts were then dried ($MgSO_4$). Solvent removal by evaporation gave colorless crystals. Recrystallization from benzene gave 3-noradamantanecarboxamide (2.36 g, 59%) as colorless crystals: Mp 186.5—187.0 °C; IR (KBr) 3415, 3201, 2924, 1651, 1617, and 1389 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.56$—1.68 (4H, m), 1.78—1.86 (4H, m), 2.00 (2H, m), 2.32 (2H, br s), 2.67 (1H, t, $J = 6.8$ Hz), 5.63 (1H, br s), and 6.28 (1H, br s); ^{13}C NMR (100 MHz) $\delta = 34.5$ (t), 37.5 (d, 2C), 43.5 (d), 43.8 (t, 2C), 47.5 (t, 2C), 54.7 (s), and 180.6 (s). Found: C, 72.96; H, 9.31%. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15%.

3-Noradamantanecarbonitrile (12). To a suspension of 3-noradamantanecarboxamide (2.42 g, 14.6 mmol) in pyridine (2.55 g, 32.3 mmol) and anhydrous 1,4-dioxane (21 ml) was added trifluoroacetic anhydride (2.28 ml, 16.1 mmol) over 15 min. After being stirred overnight at room temperature, the mixture was diluted with pentane (200 ml) and then washed with water (2×100 ml), and dried ($MgSO_4$). The solvent was carefully distilled off to give a colorless solid, which was purified by MPLC [SiO_2, hexane–ether (9 : 1)] to afford **12** (2.08 g, 96%) as colorless crystals: Mp 154.0—155.0 °C; IR (KBr) 2951, 2875, 2229, 1460, and 1090 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.53$—1.73 (4H, m), 1.87 (2H, m), 2.01 (4H, m), 2.31 (2H, br s), and 2.85 (1H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz) $\delta = 33.7$ (t), 36.8 (d, 2C), 38.7 (s), 43.2 (t, 2C), 46.1 (d), 48.0 (t, 2C), and 125.2 (s). Found: C, 81.59; H, 8.73%. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90%.

(1-Adamantyl)(3-noradamantyl)methanimine (13). A solution of 1-adamantyllithium[10)] was prepared from 1-adamantyl iodide (1.49 g, 5.70 mmol) in pentane (33 ml) and a 0.61 mol dm^{-3} solution of *t*-BuLi in pentane (10.3 ml, 6.29 mmol) at −78 °C under N_2. **12** (303 mg, 2.06 mmol) in dry pentane (5 ml) was dropwise added with stirring over 15 min, and then the mixture was stirred for 1 h. The mixture was warmed to room temperature, stirred overnight, and then water (33 ml) was cautiously added. The aqueous layer was acidified with 10% HCl and washed with hexane (2×40 ml). To the aqueous layer was immediately added 10% NaOH (40 ml). The mixture was extracted with ether (2×40 ml), and dried ($MgSO_4$). Evaporation of the solvent gave a mixture of **13** and *t*-butyl(3-noradamantyl)methanimine as colorless crystals (408 mg), which was used for the synthesis of **14** without further purification. Recrystallization from hexane gave almost pure **13** as colorless crystals: Mp 124.0—124.5 °C; IR (KBr) 2905, 1592, and 1345 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.54$—2.07 (26H, m), 2.26 (2H, br s), 2.96 (1H, t, $J = 6.6$ Hz), and 9 (1H, br s); ^{13}C NMR (100 MHz) $\delta = 28.6$ (d, 3C), 34.9 (t), 36.7 (t, 3C), 37.1 (d, 2C), 40.4 (t, 3C), 42.8 (d), 43.7 (s), 43.8 (t, 2C), 50.2 (t, 2C), 58.7 (s), and 194.0 (s).

(1-Adamantyl)(3-noradamantyl)methanone Hydrazone (14). The mixture of **13** and *t*-butyl(3-noradamantyl)methanimine (408 mg) was suspended in hydrazine hydrate (7.0 ml), to which 16 drops of sulfuric acid had been added. The mixture was refluxed for 5 d, cooled, diluted with water (150 ml), extracted with CH_2Cl_2 (6×30 ml), and dried ($MgSO_4$). Removal of the solvent followed by recrystallization from hexane gave **14** (195 mg) as colorless crystals: Mp 184.0—185.0 °C; IR (KBr) 3394, 2903, and 1454 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.53$—1.71 (11H, m), 1.84—2.03 (12H, m), 2.24—2.31 (4H, m), 3.37 (1H, t, $J = 6.6$ Hz), and 5.30 (2H, br s); ^{13}C NMR (67.8 MHz) $\delta = 29.0$ (d, 3C), 35.1 (t), 36.7 (d, 2C), 37.0 (t, 3C), 40.4 (t, 3C), 42.2 (d), 43.0 (t, 2C), 43.1 (s), 47.2 (t, 2C), 53.1 (s), and 161.1 (s). Found: C, 80.42; H, 10.35%. Calcd for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13%.

(1-Adamantyl)(3-noradamantyl)diazomethane (7). A suspension of **14** (21 mg, 0.071 mmol) and barium manganate (46 mg, 0.18 mmol) in CH_2Cl_2 (7.0 ml) was stirred under N_2 at 0 °C for 4 h in the dark. The insoluble material was removed by filtration, and evaporation of the solvent gave **7** as pale pink crystals, the purity of which was found to be 90—95% by NMR: ^{1}H NMR (270 MHz, CCl_4) $\delta = 1.75$—2.27 (25H, m), 2.45 (2H, br s), and 2.56 (1H, t, $J = 6.8$ Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) $\delta = 28.9$ (d, 3C), 32.9 (s), 34.8 (t), 36.6 (t, 3C), 37.5 (d, 2C), 41.6 (t, 3C), 43.6 (t, 2C), 44.5 (d), 46.4 (s), and 50.3 (t, 2C).

(1-Adamantyl)(3-noradamantyl)methanol (15). A solution of 1-adamantylmagnesium bromide[11)] was prepared from 1-adamantyl bromide (9.00 g, 41.8 mmol) and Mg turnings (15.3 g, 628 mmol) in dry ether (42 ml) under N_2. 3-Noradamantanecarbaldehyde (2.76 g, 18.4 mmol) in dry ether (18 ml) was dropwise added with stirring over 15 min at room temperature under N_2, and then the mixture was refluxed for 2 h. To the cooled mixture was added saturated NH_4Cl (18 ml). The aqueous layer was extracted with ether (3×13 ml), the combined extracts were washed with saturated $NaHCO_3$ (30 ml) and saturated NaCl (30 ml), and dried ($MgSO_4$). Evaporation of the solvent followed by MPLC (SiO_2, hexane–ether 9 : 1) and recrystallization from hexane afforded 2.89 g (55%) of **15** as colorless crystals: Mp 206.0—207.0 °C (lit,[28)] 251 °C decomp); IR (KBr) 3505, 2906, 1447, 1364, and 1017 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.46$—2.00 (26H, m), 2.23 (2H, br d, $J = 9.6$ Hz), 2.38 (1H, t, $J = 6.6$ Hz), and 3.10 (1H, s); ^{13}C NMR (67.8 MHz) $\delta = 28.6$ (d, 3C), 35.9 (t), 37.2 (t, 3C), 38.2 (d), 38.5 (d), 39.3 (s), 39.6 (t, 3C), 42.7 (t), 43.4 (t), 44.3 (t), 46.0 (d), 48.9 (t), 54.8 (s), and 84.1 (d). Found: C, 83.62; H, 10.52%. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56%.

(1-Adamantyl)(3-noradamantyl)methyl Methyl Ether (17). To a stirred solution of **15** (150 mg, 0.525 mmol) in dry THF (0.80 ml) cooled at 0 °C was added a solution of 1.70 mol dm^{-3} *n*-BuLi in hexane (0.32 ml, 0.55 mmol) over 5 min under N_2. The solution was stirred at 0 °C for 20 min and then MeI (297 mg, 2.10 mmol) was added over 5 min. The stirring was continued at room temperature for 17 h. After removal of the solvent, the residue was dissolved in ether (20 ml), and the insoluble material was removed by filtration. Evaporation of the ether from the filtrate gave pale yellow crystals, which on MPLC (SiO_2, hexane) afforded **17** (148 mg, 94%) as colorless crystals: Mp 108.0—109.5 °C (from hexane); IR (KBr) 2910, 2846, 1442, and 1087 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.45$—1.80 (21H, m), 1.92—1.99 (4H, m), 2.17 (2H, br s), 2.33 (1H, t, $J = 6.6$ Hz), 2.65 (1H, s), 3.54 (3H, s); ^{13}C NMR (100 MHz) $\delta = 28.6$ (d, 3C), 35.9 (t), 37.3 (t, 3C), 37.8 (d), 38.0 (d), 40.0 (t, 3C), 41.2 (s), 42.8 (t), 43.1 (t), 44.8 (d), 45.6 (t), 49.1 (t), 55.3 (s), 63.5 (q), and 96.3 (d). Found: C, 84.01; H, 10.98%. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73%.

1-Adamantyl 3-Noradamantyl Ketone. To a suspension of pyridinium chlorochromate (2.28 g, 10.6 mmol) in CH_2Cl_2 (14 ml) was added a solution of **15** (2.00 g, 6.97 mmol) in CH_2Cl_2 (14.0 ml). Then the mixture was stirred under N_2 at room temperature for 4 h. Ether (28 ml) was added and the solution was passed through a column of Florisil (7 g). Evaporation of the solvent followed by recrystallization from hexane afforded 1.69 g (85%) of 1-adamantyl 3-noradamantyl ketone as colorless crystals: Mp 176.0—177.0 °C (lit,[28)] 173 °C); IR (KBr) 2906, 1669, 1452, 1343, 1205, and 668 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.57$—2.13 (25H, m), 2.28 (2H, br s), and 2.95 (1H, t, $J = 6.7$ Hz); ^{13}C NMR (67.8 MHz) $\delta = 28.2$ (d, 3C), 35.0 (t), 36.7 (t, 3C), 37.3 (d, 2C), 38.9 (t, 3C), 42.4 (d), 43.4 (t, 2C), 47.86 (s), 47.92 (t, 2C), 62.0 (s), and 216.9 (s). Found: C, 84.27; H, 9.98%. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92%.

(1-Adamantyl)(3-noradamantyl)methyl Heptafluorobutyrate (10). To a mixture of **15** (499 mg, 1.74 mmol) and pyridine (1.74 ml) was added *n*-C_3F_7COCl (675 mg, 2.90 mmol) in CH_2Cl_2 (1.74 ml) at 0 °C over 10 min, and the resulting solution was stirred for 22 h. The reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (4×10 ml). The combined extracts were washed with saturated NaCl and dried ($MgSO_4$). Evaporation of the solvent gave colorless crystals, which on MPLC (SiO_2, hexane) afforded **10** (766 mg, 91%) as colorless crystals: Mp 80.5—81.5 °C; IR (KBr) 2915, 1773, and 1231 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.44$—1.80 (20H, m), 1.88 (1H, m), 1.95—2.04 (5H, m), 2.24 (2H, br s), and 4.93 (1H, s); ^{13}C NMR (100 MHz) $\delta = 28.2$ (d, 3C), 35.4 (t), 36.8 (t, 3C), 37.8 (d), 38.2 (d), 39.2 (t, 3C), 39.7 (s), 42.5 (t), 42.6 (t), 45.3 (t), 45.5 (d), 48.6 (t), 53.7 (s), 91.7 (d), 108.1 (tt, $J = 266$, 32 Hz, $CO\underline{C}F_2$), 108.3 (tqt, $J = 267$, 39, 34 Hz, $\underline{C}F_2CF_3$), 117.5 (qt, $J = 287$, 33 Hz, CF_3), and 158.4 (t, $J = 29$ Hz, CO). Found: C, 59.57; H, 6.03%. Calcd for $C_{24}H_{29}F_7O_2$: C, 59.75; H, 6.06%.

Formolysis of (1-Adamantyl)(3-noradamantyl)methanol (15). A solution of **15** (300 mg, 1.05 mmol) in 98% formic acid (11 ml) was refluxed for 2 h. Evaporation of the solvent afforded a colorless oil, which on MPLC (SiO_2) afforded 1,2′-biadamantyl (89 mg, 32%, hexane), 2-(1-adamantyl)-1-adamantyl formate (64 mg, 19%, hexane–ether 9 : 1), 2-(1-adamantyl)-1-adamantanol (65 mg, 22%, hexane–ether 9 : 1), and 1′, 3-diformyl-1,2′-biadamantyl (24 mg, 6%, hexane–ether 9 : 1).

1,2′-Biadamantyl: Mp 165.5—168.0 °C (lit, 166 °C,[28)] 263

°C,[7a] 266—268 °C[29]); IR (KBr) 2903, 2846, and 1448 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.19$ (1H, s), 1.53—1.72 (18H, m), 1.78—1.88 (4H, m), 1.93—2.23 (5H, m), and 2.10 (2H, s); ^{13}C NMR (100 MHz) $\delta = 27.8$ (d), 28.5 (d, 2C), 29.0 (d), 29.2 (d, 3C), 33.8 (t, 2C), 35.7 (s), 37.3 (t, 3C), 38.7 (t), 41.9 (t, 2C), 42.5 (t, 3C), and 56.0 (d).

2-(1-Adamantyl)-1-adamantyl Formate: Mp 104.5—105.5 °C; IR (KBr) 2908, 1732, 1715, and 1183 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.44$—2.26 (26H, m), 2.32 (1H, m), 2.41 (1H, br s), 2.52 (1H, d, $J = 12.2$ Hz), and 8.21 (1H, s); ^{13}C NMR (100 MHz) $\delta = 29.4$ (d, 3C), 30.4 (d), 31.1 (d), 31.6 (s), 31.9 (d, and t, 2C), 36.6 (t), 37.0 (t, 3C), 38.0 (t), 39.7 (t), 43.4 (t, 3C), 45.7 (t), 58.2 (d), 86.5 (s), and 160.7 (d).

1′,3-Diformyl-1,2′-biadamantyl: ^{1}H NMR (400 MHz) $\delta =$ 1.47—2.40 (27H, m), 2.44 (1H, d, $J = 10.8$ Hz), 8.06 (1H, s), and 8.17 (1H, s); ^{13}C NMR (100 MHz) $\delta = 30.2$ (d), 31.0 (d), 31.1 (d), 31.3 (d), 31.8 (t), 32.0 (d), 35.3 (t), 36.4 (t), 37.8 (t), 39.6 (t), 40.3 (s), 41.0 (t), 41.1 (t), 41.6 (t), 42.1 (t), 45.4 (t), 47.4 (t), 57.4 (d), 82.4 (s), 86.3 (s), and 160.3 (d, 2C).

2-(1-Adamantyl)-1-adamantanol: Mp 176.5—177.5 °C; IR (KBr) 3448, 2901, 2846, 1451, and 1084 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.34$—1.82 (20H, m), 1.95 (6H, m), 2.09 (2H, m), 2.33 (1H, br s), and 2.41 (1H, m); ^{13}C NMR (100 MHz) $\delta = 29.5$ (d, 3C), 30.2 (d), 31.2 (d), 31.4 (d), 32.1 (t), 36.4 (s), 36.9 (t), 37.2 (t, 3C), 40.1 (t), 41.5 (t), 43.8 (t, 3C), 51.7 (t), 60.1 (d), and 73.4 (s). Analytical data were unsatisfactory presumably because of the hygroscopic nature. Found: C, 82.80; H, 10.64%. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56%.

2-(1-Adamantyl)-1-methoxyadamantane (18). To a stirred solution of 2-(1-adamantyl)-1-adamantanol (48 mg, 0.17 mmol) in dry THF (0.25 ml) cooled at 0 °C was added over 5 min a solution of 1.68 mol dm^{-3} *n*-BuLi in hexane (0.11 ml, 0.18 mmol) under N_2. The solution was stirred at 0 °C for 10 min and then MeI (95 mg, 0.67 mmol) was added over 5 min. The stirring was continued at room temperature for 14 h. After removal of the solvent, the residue was dissolved in ether (2 ml), and the insoluble material was removed by filtration. Evaporation of the ether from the filtrate gave a colorless oil. MPLC (SiO_2, hexane) separation gave **18** (31 mg, 60%) as colorless crystals: Mp 88.5—91.5 °C; IR (KBr) 2902, 1448, and 1090 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.39$—1.96 (25H, m), 2.10 (2H, br s), 2.25 (1H, d, $J = 12.2$ Hz), 2.32 (1H, br s), and 3.20 (3H, s); ^{13}C NMR (100 MHz) $\delta = 30.0$ (t, 3C), 30.1 (d), 30.7 (d), 31.3 (d), 32.3 (t), 36.4 (s), 37.18 (t), 37.22 (t), 37.3 (t, 3C), 40.3 (t), 43.4 (t, 3C), 44.0 (t), 47.7 (q), 57.5 (d), and 76.9 (s). Found: C, 83.68; H, 10.99%. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73%.

2-(1-Adamantyl)-2-methoxyadamantane (25). To a stirred solution of 2-(1-adamantyl)-2-adamantanol[23] (66 mg, 0.23 mmol) in dry THF (0.35 ml) cooled at 0 °C was slowly added a solution of 1.68 mol dm^{-3} *n*-BuLi in hexane (0.14 ml, 0.24 mmol) over 5 min under N_2. The solution was stirred at 0 °C for 10 min and then MeI (130 mg, 0.93 mmol) was added over 5 min. The stirring was continued at room temperature for 13 h. After removal of the solvent, the residue was dissolved in ether (2 ml), and the insoluble material was removed by filtration. Evaporation of the ether from the filtrate gave colorless crystals. The products were subjected to NMR analysis.

25: ^{1}H NMR (400 MHz) $\delta = 3.39$ (s, 3H); ^{13}C NMR (100 MHz) $\delta = 27.3$, 27.7, 29.5 (3C), 33.7 (2C), 34.9 (2C), 36.0 (2C), 37.1 (3C), 39.7, 40.2 (3C), 42.0, 51.5, 81.9.

Methanolysis of (1-Adamantyl)(3-noradamantyl)methyl Heptafluorobutyrate (10). A solution of **10** (457 mg, 0.946 mmol) in methanol (23.7 ml) containing 0.050 mol dm^{-3} 2,6-lutidine was heated in a constant temperature oil bath (100 °C) for 7.0 h (10 half-lives). After most of the methanol had been removed at 0 °C under vacuum, the residue was dissolved in ether. This solution was washed with 10% NaCl, cold 5% HCl, 10% NaCl, 5% $NaHCO_3$, and saturated NaCl, and dried ($MgSO_4$). Evaporation of the ether afforded a faintly yellow oil. The oil was subjected to NMR analysis, by which product yields were determined. MPLC (SiO_2) separation afforded 4-(1-adamantyl)-3-methoxyprotoadamantane (**19**, 71 mg, hexane), 2-(1-adamantyl)-1-methoxyadamantane (**18**, 168 mg, hexane), and a mixture of ethers **17**, **18**, and **19** as colorless crystals.

4-(1-Adamantyl)-3-methoxyprotoadamantane (19): Colorless crystals; mp 118.0—119.0 °C; IR (KBr) 2895, 1466, 1102, and 1081 cm^{-1}; ^{1}H NMR (400 MHz) $\delta = 1.23$—1.38 (4H, m), 1.60—2.00 (22H, m), 2.06 (1H, m), 2.19 (1H, br s), 2.26 (1H, br t, $J = 5.6$ Hz), and 3.17 (3H, s); ^{13}C NMR (100 MHz) $\delta = 28.6$ (d), 29.2 (d, 3C), 30.2 (t), 33.3 (t), 36.2 (d), 37.5 (t, 3C), 39.0 (t), 39.3 (t), 39.8 (t), 40.2 (d), 41.4 (t, 3C), 45.8 (d), 49.7 (q), and 89.2 (s). Found: C, 83.79; H, 10.96%. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73%.

Methanolysis of (1-Adamantyl)(3-noradamantyl)diazomethane (7). A degassed solution of **7** in methanol was stirred at 0 °C. The stirring was continued at room temperature for 12 h. After removal of the solvent, the residue was dissolved in $CDCl_3$ and subjected to NMR analysis, by which product yields were determined.

Photolysis of (1-Adamantyl)(3-noradamantyl)diazomethane (7). A degassed solution of **7** in hexane–methanol was irradiated at 0 °C under the conditions specified in Table 3. After removal of the solvent, the mixture was analyzed by NMR, by which product yields were determined. The photolysis in hexane and cyclohexane was conducted in a similar manner. Separation by high performance liquid chromatography gave **20** as colorless crystals.

2-(1-Adamantyl)-2,4-didehydroadamantane (20): ^{1}H NMR (400 MHz) $\delta = 2.00$—1.25 (26H, m), 2.21(1H, br s), and 2.34 (1H, br s); ^{13}C NMR (100 MHz); $\delta = 20.2$ (d), 24.2 (d), 26.3 (d), 28.6 (d, 3C), 29.4 (t), 32.5 (d), 33.0 (t), 33.2 (s, and d, 2C), 34.2 (t), 37.3 (t, 3C), 39.0 (t, 3C), 43.6 (s), and 50.3 (t). HRMS Found: *m*/*z* 268.2182. Calcd $C_{20}H_{28}$: M, 268.2191.

Kinetic Procedure. The kinetic methods were described previously.[30] All measurements were conducted in the presence of 0.025 mol dm^{-3} 2,6-lutidine with 0.01 mol dm^{-3} substrate concentrations for titrimetric measurements. The first-order rate constants were calculated by the least-squares method.

Calculations. Empirical molecular mechanics calculations were performed through the MM2(87) program[17] on a FACOM M1800 computer and the MM3(92) program[18] on an IBM RS/6000 computer.

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