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Generation and Reactivity of 2-Substituted Adamantenes

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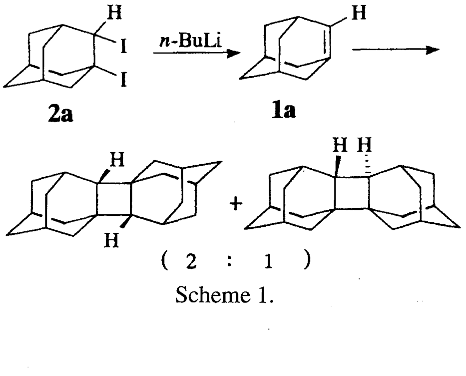
The title bridgehead olefins, generated by the dehalogenation of 1,2-dihalo-2-R-adamantanes (R = Me, Et, Ph, p-$CF_3C_6H_4$) with excess t-BuLi, yielded 2-t-butyl-2-R-adamantanes (**15**), 1-t-butyl-2-R-adamantanes (**16**), and dimeric products. The ratios of the yields (%) of **16** to **15** were 20 : 3 (R = Me), 32 :< 1 (R = Et), 4 : 60 (R = Ph), and 5 : 57 (R = p-$CF_3C_6H_4$). 2-Alkyladamantenes predominantly yielded the products t-butylated at C(1), whereas 2-aryladamantenes gave the products t-butylated at C(2). The total yields of the dimers decreased with the bulkiness of substituents at position C(2). The dimerization of 2-methyladamantene gave a head-to-head dimer, 1-(2-methyl-1-adamantyl)-2-methyleneadamantane, as well as a head-to-tail dimer, 1-(2-methyl-2-adamantyl)-2-methyleneadamantane. The [4+2] cycloaddition between two molecules of 2-phenyladamantene, in which the phenyl group participates as a part of the diene, yielded a dimer of the head-to-tail type.

These results suggest that: i) a substituent at position C(2) can kinetically stabilize 2-R-adamantene and suppress the dimerization, ii) 2-alkyladamantenes might have a biradical nature, and iii) the regioselective [4+2] cycloaddition and t-BuLi addition of 2-phenyladamantene in THF can be explained by assuming a certain contribution of zwitterionic nature in the double bond that may be dependent on the media and nucleophiles.

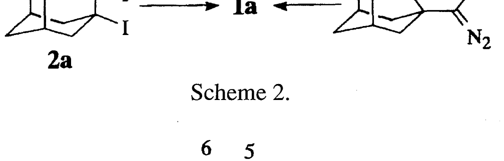
The synthesis and properties of *anti*-Bredt olefins have long fascinated organic chemists.1) Recent progress in cubene2) and homocubene3,4) chemistry appears to be opening up a new era in this field. Adamantene (**1a**) is one of the most unstable strained bridgehead olefins, and has been extensively studied, and suggested to have a biradical nature by several groups.5—9) McKervey et al.5) and Lenoir and Firl6) independently studied the reaction of **1a**, which was generated by the treatment of 1,2-diiodoadamantane (**2a**) with excess butyllithium in solution, and found that **1a** gave two dimers having the formula $C_{20}H_{28}$ in remarkably high yields (Scheme 1). To the dimers were assigned structures having cyclobutanes formed by the [2+2] dimerization of **1a**. It was specifically noted that furan was totally ineffective in trapping adamantene, since no Diels–Alder adduct could be isolated.

Michl et al.7) generated **1a** by treating **2a** with Na, observed its IR and UV spectra in argon or nitrogen matrix, and concluded that the carbon–carbon double bond is markedly twisted and weakened. Recently, Jones, Jr., et al.8) presented further evidence concerning the proposal that the McKervey dehalogenation route produces **1a**, and that **1a** has a biradical character, by comparing the products of the carbene route with those of dehalogenation in the gas phase (Scheme 2).

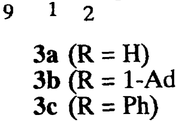


Scheme 1.

On the other hand, in the long history of *anti*-Bredt olefins, there can be found only a few studies related to the effect of a substituent at the vinylic position based on the nature of the double bond. 3-Homoadamantene (tricyclo[4.3.1.1^{3,8}]undec-3-ene: **3a**), prepared by Schleyer et al.,10) was characterized by infrared spectroscopy performed on a NaCl plate at −196 °C, but dimerized upon warming to −20 °C (Scheme 3). Replacing the vinyl hydrogen in **3a** with a bulky 1-adamantyl group to form 4-(1-



Scheme 2.

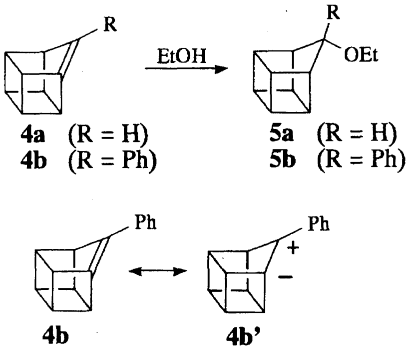


3a (R = H)
3b (R = 1-Ad)
3c (R = Ph)
3d (R = COOMe)

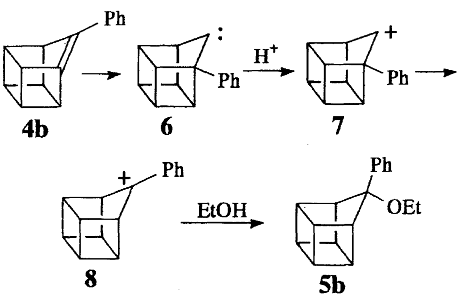
Scheme 3.

adamantyl)-3-homoadamantene (**3b**) inhibited dimerization, and remarkably enhanced the thermal stability.[10] Eaton et al.[4] studied the generation and reactivity of 9-phenyl-1(9)-homocubene (**4b**), and suggested that the regiospecific addition of ethanol on the twisted double bond of **4b** to give 9-ethoxy-9-phenylhomocubane (**5b**) is due to a zwitterionic nature (**4b′**) (Scheme 4). However, there remains a question whether the phenyl group really enhances a zwitterionic nature (**4b′**), since the direction of ethanol addition is similar to that observed in the reaction of the parent 9(1)-homocubene (**4a**).[3c,3d,3f,3g] In addition, if 1-phenyl-9-homocubylidene (**6**), to which **4b** rearranges, is protonated, the resulting cation (**7**) would smoothly rearrange to 9-phenyl-9-homocubyl cation (**8**), and could subsequently give **5b** (Scheme 5).[3c,11] Wiberg and Waddell[12] generated 2-phenylbicyclo [2.1.1]hex-1-ene (**9**), and found that it reacts with ethanol to give 2-ethoxy-2-phenylbicyclo[2.1.1]hexane (**10**) (Scheme 6). However, the mechanism for the formation of **10** is not clear. Eguchi et al.[13] reported the generation of 4-phenyl-3-homoadamantene (**3c**) and 4-methoxycarbonyl-3-homoadamantene (**3d**) by a carbene route and their synthetic application, and suggested that the 4-phenyl group stabilizes 3-homoadamantene.

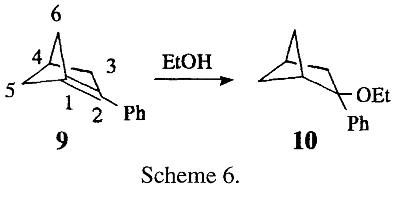
With such a background, the introduction of a substituent at C(2) in adamantene (**1a**) was expected to inhibit dimerization and to enhance the kinetic stability, owing to protection of the double bond.[14] We wished to investigate the effect of alkyl and aryl substituents on the kinetic stability and the reaction behaviors of 2-R-adamantenes [**1b** (R = Me), **1c** (R = Et), **1d** (R = Ph), and **1e** (R = p-$\mathrm{CF_3C_6H_4}$)], which were generated by McKervey's dehalogenation route (Scheme 7). Although we were unable to directly observe olefins **1b**—**e** by NMR at low temperatures, a study of their reaction with excess t-BuLi and dimerization revealed a biradical nature of 2-alkyladamantenes (**1b** and **1c**) and a regioselective reaction of 2-aryladamantenes (**1d**—**e**), as well as the ability of a substituent at position C(2) to suppress dimerization. The reaction behavior of 2-aryladamantenes (**1d** and **1e**) can be explained by a certain contribution of the zwitterionic nature in the double bond.



Scheme 4.



Scheme 5.



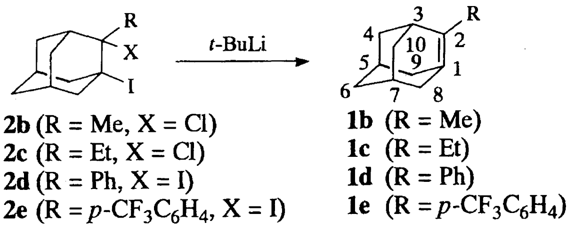
Scheme 6.

Results and Discussion

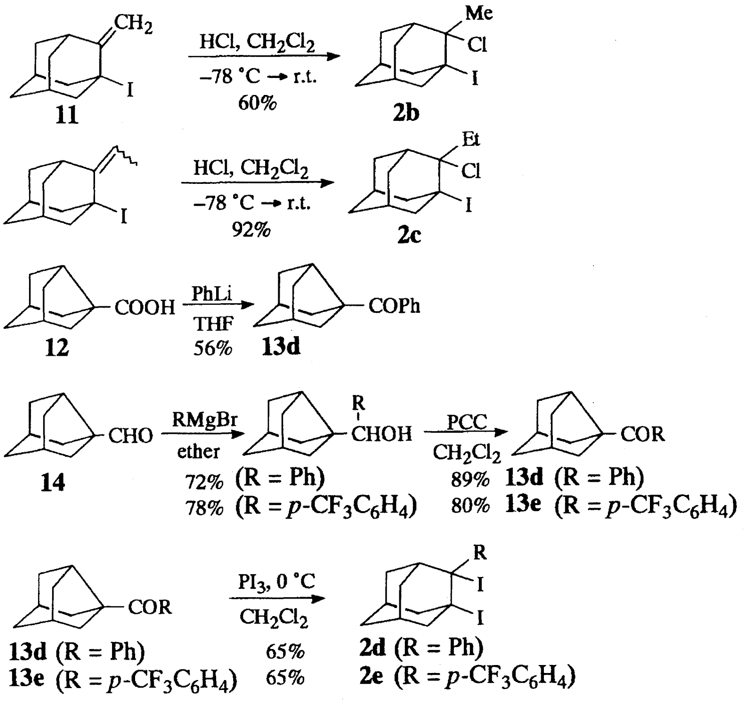
Synthesis of the Precursors of 2- Substituted Adamantenes (1b—e). The synthesis of 2-substituted 1,2-dihaloadamantanes (**2b**—**e**) is shown in Scheme 8. Hydrochlorination of 1-iodo-2-methyleneadamantane (**11**)[15a,15b] gave 2-chloro-1-iodo-2-methyladamantane (**2b**). 2-Chloro-2-ethyl-1-iodoadamantane (**2c**) was synthesized as reported previously.[15a,15c] 3-Noradamantyl phenyl ketone (**13d**) was obtained by the reaction of 3-noradamantanecarboxylic acid (**12**) with phenyllithium. 3-Noradamantyl p-(trifluoromethyl)phenyl ketone (**13e**) was prepared by the reaction of 3-noradamantanecarbaldehyde (**14**) with p-(trifluoromethyl)-phenylmagnesium bromide, followed by pyridinium chlorochromate (PCC) oxidation. Ketones **13d** and **13e** gave **2d** and **2e** by a reaction with $\mathrm{PI_3}$ in $\mathrm{CH_2Cl_2}$ at 0 °C, respectively.

^{13}C labeled 1,2-diiodo-2-phenyladamantane (**[2-^{13}C]-2d**) was prepared by a method similar to that used for the synthesis of an unlabeled compound from 3-noradamantane[^{13}C]-carboxylic acid (**[^{13}C]-12**), which was synthesized by the reaction of $^{13}\mathrm{CO_2}$ with 3-noradamantyllithium (Scheme 9).[16]

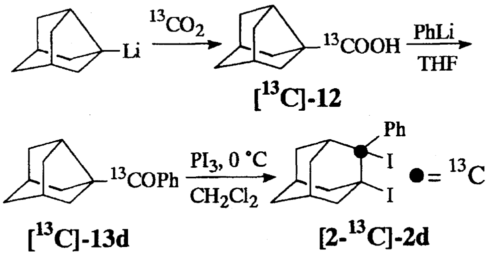
Dehalogenation of 2-Chloro-1-iodo-2-methyladamantane (2b) with t-BuLi. To a solution of **2b** in THF at −110 °C was dropwise added two molar amounts of t-BuLi in pentane. The mixture was quenched with methanol, and product distribution was determined by gas chromatography (GC) and NMR analysis. The results of a product analysis are summarized in Scheme 10. The product mixture was divided into monomeric products and dimers by preparative GC separation. The obtained monomeric products were separated into 1-t-butyl-2-methyleneadamantane (**17b**) as colorless crystals and a mixture of 2-t-butyl-2-methyladamantane (**15b**) and 1-t-butyl-2-methyladamantane (**16b**) by high performance liquid chromatography (HPLC). The identification



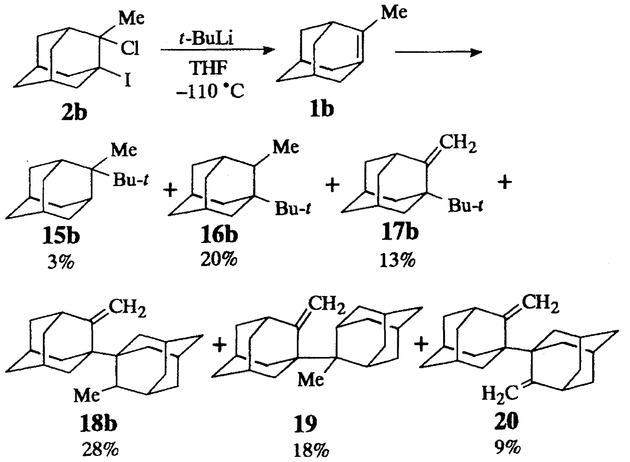
Scheme 7.



Scheme 8.



Scheme 9.

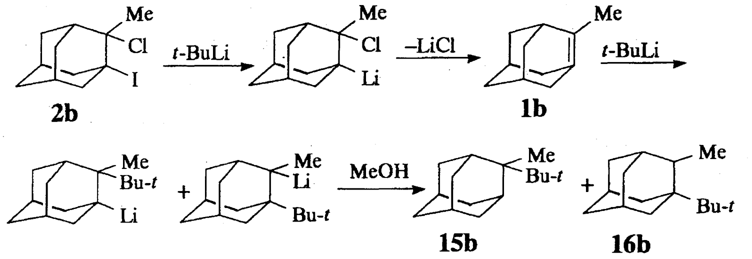


Scheme 10.

of **15b** and **17b**, which have C_s symmetry, and **16b**, which has C_1 symmetry, rested on the NMR spectra. HPLC separation of the dimers gave 2,2′-dimethylene-1,1′-biadamantane (**20**) as colorless crystals and a mixture of 1-(2-methyl-1-adamantyl)-2-methyleneadamantane (**18b**) and 1-(2-methyl-2-adamantyl)-2-methyleneadamantane (**19**). The structures of the dimers were determined based on the close similarity of the NMR signals of their 2-methyl-2-adamantyl, 2-methyl-1-adamantyl, and 2-methylene-1-adamantyl moieties with those of **15b**, **16b**, and **17b**, respectively. GC high-resolution mass spectrometric experiments were consistent with the chemical formulas of **15b** ($C_{15}H_{26}$), **16b** ($C_{15}H_{26}$), **17b** ($C_{15}H_{24}$), **18b** ($C_{22}H_{32}$), **19** ($C_{22}H_{32}$), and **20** ($C_{22}H_{30}$).

The most probable mechanism of the reaction is shown in Scheme 11. Based on the expectation that the iodine in **2b** would be more reactive toward *t*-BuLi than the chlorine, lithium–iodine exchange is considered to occur first to give 2-chloro-2-methyl-1-adamantyllithium, and a subsequent elimination of LiCl gives 2-methyladamantene (**1b**). The addition of *t*-BuLi to the double bond gives *t*-butyladamantyllithiums, and a subsequent proton transfer from MeOH yields **15b** and **16b**. A similar mechanism for the generation of bridgehead olefins and alkyllithium addition has been reported in many examples.[1]

The possibility of the direct formation of *t*-butyladamantyl halide from **2b** and a subsequent lithium–halogen exchange may be excluded, since it has been reported that the reaction of haloadamantanes with butyllithium gives no butyladamantanes.[6,17] In the dehalogenation of **2b** with one molar amount of *t*-BuLi, the same products were obtained in a similar ratio. However, approximately half of dihalide **2b** remained unchanged and no products which would be formed by removal of only one halogen atom could be detected. These results support the idea that the direct alkylation of **2b** can be neglected. The difficulty in direct alkylation also suggests that **17b** is formed not through 2-methylene-1-adamantyl iodide, which might be formed from **2b**, but through 1-*t*-butyl-2-methyl-2-adamantyllithium, which is formed by the addition of *t*-BuLi to **1b**.

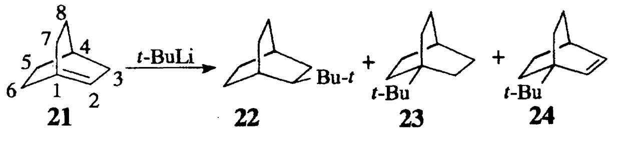


Scheme 11.

The formation of analogous products from bicyclo[2.2.2]oct-1-ene (**21**) has been reported by Bickelhaupt et al.[18] The reaction of **21** with *t*-BuLi gives 2-*t*-butyl- and 1-*t*-butylbicyclo[2.2.2]octanes, and 1-*t*-butylbicyclo[2.2.2]oct-2-ene (Scheme 12). They have suggested that **21** has a biradical nature on the basis of the formation of these products.

There are two possible routes for the formation of dimers **18b** and **19**. One is the [2+2] dimerization of 2-methyladamantene (**1b**) followed by opening of the cyclobutane ring and a subsequent intramolecular hydrogen shift. The other is a direct formation of 1,4-biradicals, owing to the biradical nature of **1b**, and subsequent intramolecular hydrogen shift (Scheme 13). We prefer the latter mechanism, since the steric hindrance to the [2+2] dimerization would be significant.

The ratio of **15b** to **16b** was 3 : 20 (Scheme 10). The predominant formation of adduct **16b** would be due to the steric effect of the alkyl substituent in the addition of *t*-BuLi. MM2(87) calculations[19] show that **15b** is more strained than **16b** by 43.6 kJ mol^{-1} (Table 1), suggesting that the steric effect of the alkyl substituent has an important role in the addition of *t*-BuLi. The relatively low selectivity observed in the dimerization might be attributed to a biradical nature of 2-methyladamantene (**1b**). The ratio of **18b** to **19** was 28 : 18, and the head-head adduct was formed more than the head-tail one. This ratio does not conflict with the results of the MM2 calculations, showing that **19** is more strained than **18b** by 44.1 kJ mol^{-1}.



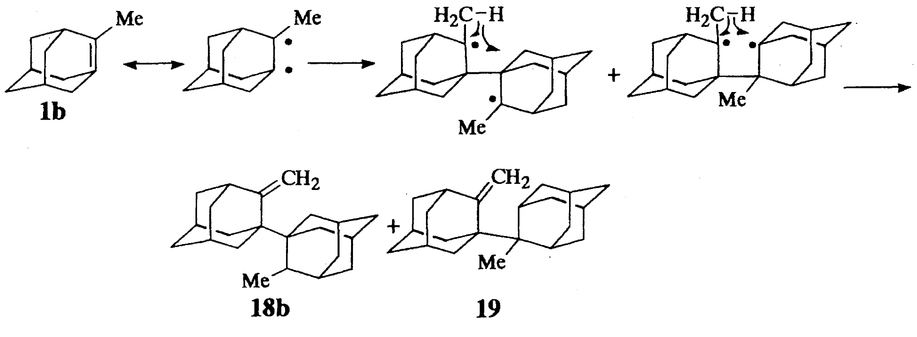
Scheme 12.

Table 1. Strain Energy (SE) of 2-*t*-Butyl- and 1-*t*-Butyl-2-R-adamantanes [**15b** and **16b** (R = Me), **15d** and **16d** (R = Ph)] and 1-(2-Methyl-2-adamantyl)- and 1-(2-Methyl-1-adamantyl)-2-methyleneadamantanes (**18b** and **19**) Calculated by MM2(87)

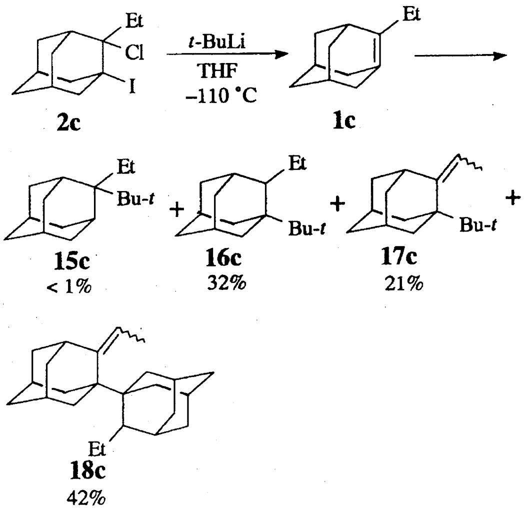
Compd	SE/kJ mol^{-1}	ΔSE/kJ mol^{-1}
16b	102.7	
15b	146.3	43.6[a]
18b	182.6	
19	226.7	44.1[b]
16d	115.6	
15d	147.8	32.2[c]

a) Difference between strain energies of **16b** and **15b**. b) Difference between strain energies of **18b** and **19**. c) Difference between strain energies of **16d** and **15d**.

Dehalogenation of 2-Chloro-2-ethyl-1-iodoadamantane (2c) with *t*-BuLi. To a solution of **2c** in THF at −110 °C was dropwise added two molar amounts of *t*-BuLi in pentane. The mixture was quenched with methanol, and the product distribution was determined by NMR analysis (Scheme 14). Medium-pressure liquid chromatography (MPLC) separation gave 1-*t*-butyl-2-ethyladamantane (**16c**) as a colorless oil and a mixture of 1-*t*-butyl-2-ethylideneadamantane (**17c**) and 1-(2-ethyl-1-adamantyl)-2-ethylideneadamantane (**18c**). The structures of **16c** and **17c** were determined by a comparison of their NMR spectra with those of **16b** and **17b**, respectively. Dimeric product **18c** was identified by a comparison of its spectroscopic data with those of **16c** and **17c**. The GC high-resolution mass spectra exhibited signals of $C_{16}H_{28}$, $C_{16}H_{26}$, and $C_{24}H_{36}$ for **16c**, **17c**, and **18c**, respectively. The yield of the dimer from 2-ethyladamantene (**1c**) was lower than that from 2-methyladamantene (**1b**). This result suggests that the bulkiness of the alkyl substituent at position C(2) kinetically



Scheme 13.

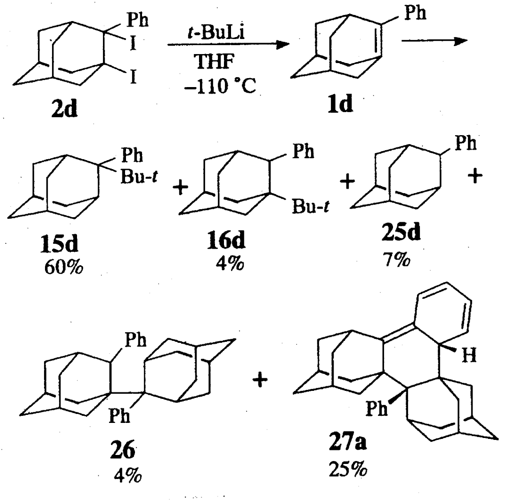


Scheme 14.

stabilizes **1** and suppresses dimerization.

Dehalogenation of 1,2-Diiodo-2-phenyladamantane (2d) with *t*-BuLi. To a solution of **2d** in THF at −110 °C was added three molar amounts of *t*-BuLi in pentane. After an aqueous work-up, the product distribution was determined by an NMR analysis (Scheme 15). Each product (except for **16d** and **25d**) was separated by MPLC. The reaction was found to give mainly five products (2-*t*-butyl-2-phenyladamantane (**15d**), 1-*t*-butyl-2-phenyladamantane (**16d**), 2-phenyladamantane (**25d**),[20] and two dimers (**26** and **27a**[21])). In the ^{13}C NMR spectrum of **15d**, which has C_s symmetry, there are only resonances for seven different kinds of adamantyl carbons, along with two expected for the *t*-butyl group and four expected for the phenyl group. The NMR spectra of **16d** were identical to those of an authentic sample. The GC high-resolution mass spectrometric analysis of **16d** was consistent with its proposed molecular formula. The signals of ^{13}C NMR of **25d** agreed with those reported in the literature.[20,22] The determination of the structures of **26** and **27a** is discussed later.

When one molar amount of *t*-BuLi was used to generate **1d**, the above-mentioned products were formed in a similar ratio, and about half of **2d** was recovered. No formation of **15d′** and **16d′**, whose structures are shown in Scheme 16, indicates that **2d** undergoes dehalogenation much faster than direct *t*-BuLi addition to give **15d′** and **16d′**. Therefore, the possibility of the formation of **15d** and **16d** through **15d′** and **16d′** can be neglected.[23]

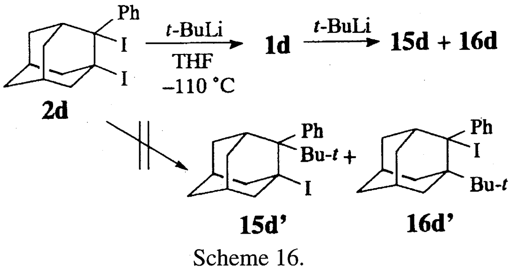


Scheme 15.

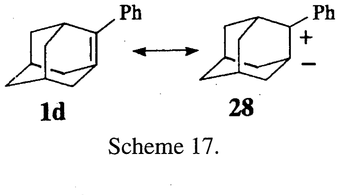
Interestingly, the ratio of **15d** to **16d** was 60 : 4. The product butylated at the bridge position dominated the other, unlike in the cases of 2-alkyladamantenes (**1b** and **1c**). MM2(87) calculations (Table 1) show that **15d** is more strained than **16d** by 32.2 kJ mol^{-1}, indicating that the more congested adduct **15d** was predominantly formed. If 2-phenyladamantene (**1d**) is hypothesized to have a nature of zwitterionic state **28** (Scheme 17), the reversed selectivity of *t*-BuLi addition can be explained. We have recently reported that **1d**, generated by photolysis of 1-(3-noradamantyl)-1-phenyldiazomethane (Scheme 18) in benzene, is trapped by oxygen and tri(*n*-butyl)tin hydride much faster than by methanol, demonstrating a biradical character.[21] The present results, however, suggest that there is also a certain contribution of the zwitterionic state in THF. It appears that the reaction behavior of **1d** is changed by the media and nucleophiles.

The yields of the two dimeric products were 4% (**26**) and 25% (**27a**). Dimer **26** was identified to be 2,2′-diphenyl-1,2′-biadamantane by a comparison of its spectroscopic data with those of **15d** and **16d**. This identification was consistent with the results of high-resolution mass spectrometry. 2,2′-Diphenyl-1,1′-biadamantane, which is a head-to-head dimer and an isomer of **26**, was not detected, unlike the reactions of adamantene (**1a**) and 2-methyladamantene (**1b**), which gave the two isomeric dimers (Schemes 1 and 10).

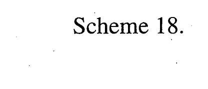
The high-resolution mass spectrum indicates that the molecular formula of **27a** is $C_{32}H_{36}$, which corresponds to two molecules of **1d**. The ^{13}C NMR spectrum showed signals of twenty aliphatic carbons and twelve olefinic and aromatic carbons, and the ^{1}H NMR spectrum showed aliphatic



Scheme 16.



Scheme 17.



Scheme 18.

protons, four olefinic protons, and five aromatic protons (Table 2). The absorption maximum observed in the electronic spectrum of **27a** [λ_{max} (benzene) 327 nm] is close to that (313 nm) predicted by Woodward's rule[24] for the 5-isopropylidene-1,3-cyclohexadiene structure. These spectroscopic data agree with the assignment that **27a** is an intermolecular [4+2] cycloaddition product.[25]

The [4+2] cycloaddition of **1d** has the possibility of yielding isomers of head-to-tail (**27a**, **27b**) and head-to-head types (**29**) (Scheme 19). The carbon skeleton of the obtained adduct was determined by analyzing the ^{13}C NMR of the products from 1,2-diiodo-2-phenyladamantane labeled by ^{13}C (98.5%) at the C(2) position (**[2-^{13}C]-2d**). If the dimer is **[^{13}C]-27a**, the carbon at C(1) should be observed as a doublet–doublet peak, owing to two adjacent ^{13}C labels (C(2) and C(2′));[26] however, if **[^{13}C]-29**, this carbon should be observed as a doublet peak. A partial assignment of the signals in the ^{13}C NMR spectrum of the dimer from **[2-^{13}C]-2d** is shown in Fig. 1. The signals at δ = 37.5 and 45.4 for quaternary bridgehead carbons were observed as a doublet and a doublet–doublet, respectively. These observations can be reasonably explained by structure **27a**.

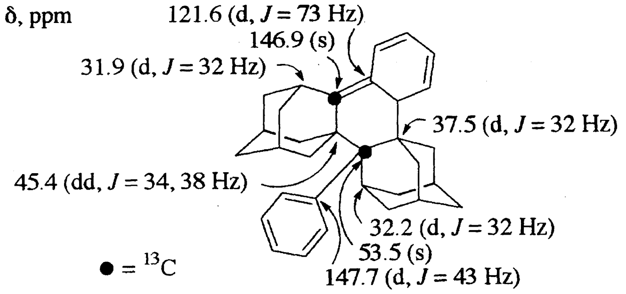


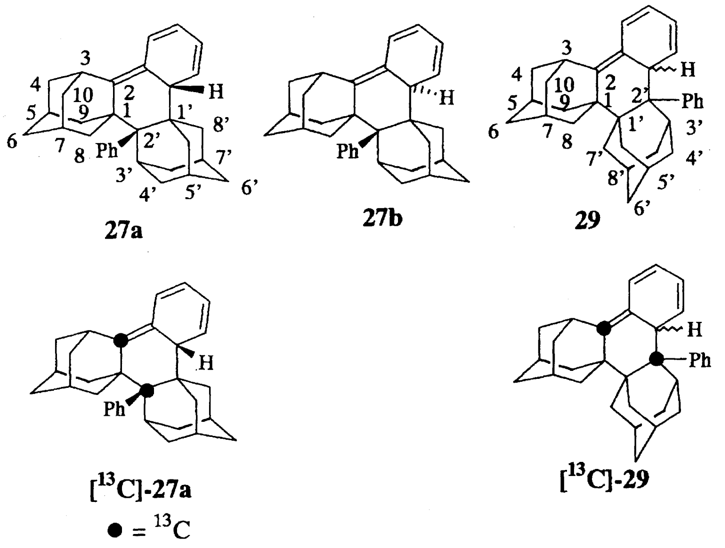
Fig. 1. A partial assignment of ^{13}C NMR of **[^{13}C]-27a**. (The multiplicities of signals and their coupling constants were shown in the parentheses. Very large signals were observed at 146.9 and 53.5 ppm. The signals at 31.9 and 32.2 ppm are interchangeable.)

Dimer **27a** has a diastereomer **27b**. MM3[27] calculations show that compound **27a** is less strained than **27b** by 24 kJ mol^{-1} (Table 3), suggesting that the obtained dimer is **27a**. The barrier to the rotation of the phenyl group in **27a** was calculated to be higher than 150 kJ mol^{-1} (Figs. 2 and 3), which suggests that the rotation in **27a** should be frozen at room temperature. This point agrees with the result that all aromatic carbons showed different ^{13}C chemical shifts (Table 2). The proton H$_A$ of **27a** in Fig. 2 is predicted to be shielded by the phenyl ring[28] and observed as a doublet–triplet signal in ^{1}H NMR. In fact, one pair of the methylene proton signals was observed at δ = 0.28 and 1.17, which can be assigned to protons H$_A$ and H$_E$, respectively.

In the most probable dimerization mechanism, shown in Scheme 20, olefin **1d** dimerizes to give intermediate **30**,

Table 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR Spectral Data for **27a** in CDCl$_3$

^{1}H NMR	δ = 0.28 (1H, dt, J = 13, 3.2 Hz), 1.17 (1H, dt, J = 13, 3.2 Hz), 1.34 (1H, d, J = 11 Hz), 1.48 (1H, d, J = 12 Hz), 1.54—1.88 (12H, m), 2.05 (2H, br s), 2.16 (1H, d, J = 11 Hz), 2.32 (1H, d, J = 14 Hz), 2.58—2.78 (4H, m), 2.85 (1H, br d, J = 14 Hz), 3.28 (1H, br s), 4.04 (1H, br s), 5.88 (1H, m), 6.02 (1H, m), 6.08 (1H, d, J = 12 Hz), 6.57 (1H, d, J = 12 Hz), 7.1—7.3 (4H, m), 7.37 (1H, d, J = 8.4 Hz).
^{13}C NMR	δ = 28.0 (CH), 29.27 (CH), 29.33 (CH), 30.0 (CH), 31.9 (CH), 32.2 (CH), 35.5 (CH$_2$), 36.2 (CH$_2$), 37.2 (CH$_2$), 37.5 (C), 37.6 (CH$_2$), 38.1 (CH$_2$), 39.1 (CH$_2$), 39.87 (CH$_2$), 39.92 (CH$_2$), 43.4 (CH$_2$), 45.4 (C), 46.7 (CH), 50.3 (CH$_2$), 53.5 (C), 121.6 (C), 122.1 (CH), 122.3 (CH), 123.7 (CH), 124.7 (CH), 126.2 (CH), 127.7 (CH), 130.4 (CH), 130.6 (CH), 132.1 (CH), 146.9 (C), 147.7 (C).



Scheme 19.

Table 3. Heat of Formation (ΔH_f) and Strain Energy (SE) of Dimers (**27a** and **27b**) of 2-Phenyladamantene (**1d**) Calculated by MM3(92)

Compd	ΔH_f/kJ mol^{-1}	SE/kJ mol^{-1}
27a	257.4	229.6
27b	281.5	254.0

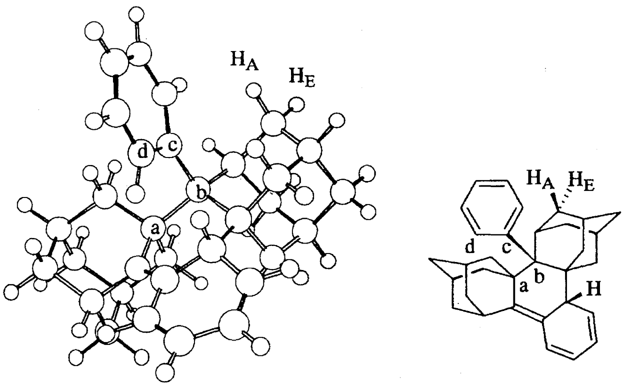


Fig. 2. MM3(92) optimized structure of **27a**.

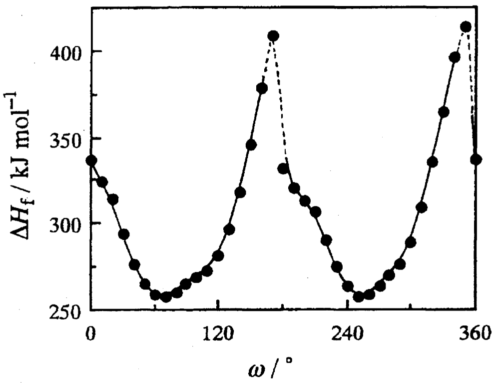
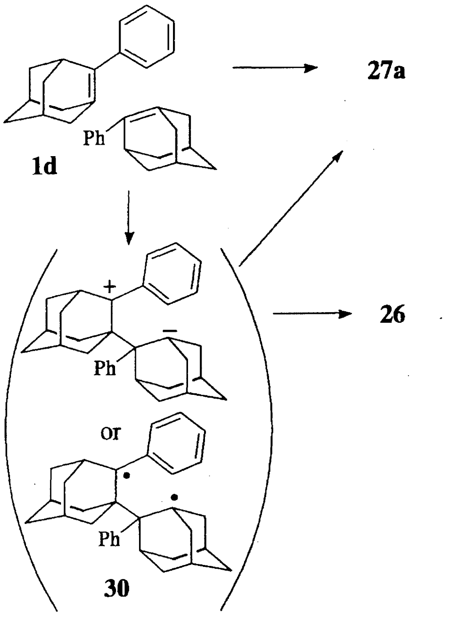


Fig. 3. Plot of heat of formation (ΔH_f) of **27a** against dihedral angle (ω) of C_a–C_b–C_c–C_d in Fig. 2.

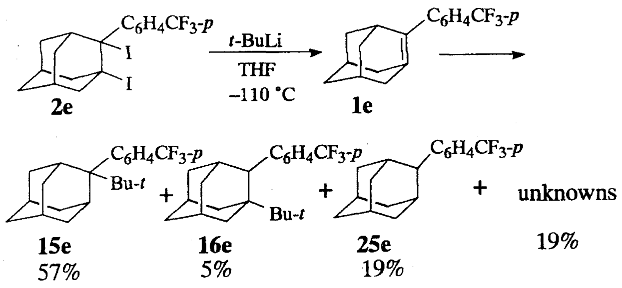
which yields dimers **26** and **27a**.[22] Many examples of the cycloaddition of styrene analogues with dienophiles have been reported,[29] in which a phenyl group is involved as a part of a diene. **1d** gave only **27a**, which is regarded as being a kind of the head-to-head dimer; and other possible [4+2] dimers (**27b** and **29**) were not detected. The selectivity in the [4+2] cycloaddition would be caused by factors similar to those in the butylation of **1d**.[4,13]

Attempts to trap **1d** with 1,3-butadiene and diphenylisobenzofuran were unsuccessful.

Dehalogenation of 1,2-Diiodo-2-[*p*-(trifluoromethyl)-phenyl]adamantane (2e) with *t*-BuLi. The dehalogenation of **2e** with three molar amounts of *t*-BuLi gave 2-*t*-butyl-2-[*p*-(trifluoromethyl)phenyl]adamantane (**15e**), 1-*t*-butyl-2-[*p*-(trifluoromethyl)phenyl]adamantane (**16e**), 2-[*p*-(trifluoromethyl)phenyl]adamantane (**25e**), and unknown products in a ratio 57 : 5 : 19 : 19 (Scheme 21). The structures of **15e** and **16e** were determined by considering their symmetry and a comparison of their NMR data with those for the phenyl substituted compounds (**15d** and **16d**). The spectral data for **25e** agreed with those of the authentic sample.



Scheme 20.

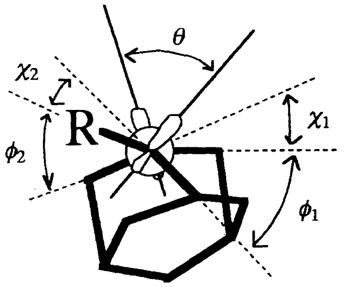


Scheme 21.

The ratio of **15e** to **16e** is 57 : 5, which is similar to that of **15d** to **16d** in the reaction of **1d**. The trifluoromethyl group has a slight influence on the regioselectivity of butylation. If **1d** has an enhanced zwitterionic nature, then **1e**, which has an electron-withdrawing group, is expected to show a much different reaction behavior from that of **1d**. This result suggests that the emerged zwitterionic nature in **1d** and **1e** is small.

Calculations. The distortion at the π bonds in *anti*-Bredt olefins is similar to that suffered by *trans*-cycloalkenes.[1] The loss of the π-bond energy due to twisting of the double bond is partially recovered by rehybridization of the π center, particularly the C(2) carbon, the consequence of which is pyramidalization. In Fig. 4, the angles χ_1, χ_2, ϕ_1, and ϕ_2 are defined by two distinct types of the out-of-plane deformations of the double bond, i.e. out-of-plane bending (χ_1 and χ_2) and pure twisting (ϕ_1 and ϕ_2).[1] The angle of pure twisting of the p orbitals (θ) is defined as $(\phi_1 + \phi_2)/2$.[1]

The structural deformation concerning 2-substituted adamantenes **1**, calculated by the MM2[19] and PM3[30] methods, is given in Tables 4 and 5, respectively. The optimized geometries of adamantene (**1a**), 2-methyladamantene (**1b**) and 2-phenyladamantene (**1d**) have dihedral angles (θ) be-



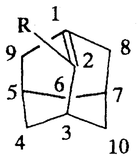


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Fig. 4. Two distinct types of the out-of-plane deformations of double bond of **1** (out of plane bending, χ_1 and χ_2, pure twisting, ϕ_1 and ϕ_2, and angle of pure twisting of p orbitals, θ).

Table 4. Results of MM2(87) Calculations for 2-R-adamantenes [**1a** (R = H), **1b** (R = Me), and **1d** (R = Ph)]

Compd	R	$\theta/^\circ$	$\chi_1/^\circ$	$\chi_2/^\circ$	$\phi_1/^\circ$	$\phi_2/^\circ$	C(1)–C(2)bond/Å
1a	H	55.6	56.0	64.9	60.0	51.2	1.354
1b	Me	66.7	63.9	41.6	55.6	77.9	1.355
1d	Ph	68.7	63.7	33.5	53.6	83.8	1.364

Table 5. Results of PM3 Calculations for 2-R-adamantenes [**1a** (R = H), **1b** (R = Me), **1c** (R = Et), **1d** (R = Ph), and **1e** (R = p-$CF_3C_6H_4$)]

Compd	R	$\theta/^\circ$	$\chi_1/^\circ$	$\chi_2/^\circ$	$\phi_1/^\circ$	$\phi_2/^\circ$	C(1)–C(2) bond/Å
1a	H	55.1	44.0	35.3	50.7	59.5	1.370
1b	Me	60.7	44.3	27.8	52.5	68.9	1.378
1c	Et	60.5	44.1	28.0	52.5	68.6	1.378
1d	Ph	61.9	43.4	27.0	53.5	70.1	1.385
1e	p-$CF_3C_6H_4$	62.1	42.6	27.3	54.4	69.7	1.386

tween the double-bond p orbitals of 56°, 67°, and 69° by MM2 and 55°, 61°, and 62°, respectively, by PM3. The double bonds in **1b** and **1d** are more twisted than the bond in **1a**. The angles of pyramidalization (χ_2) at C(2) for **1a**, **1b**, and **1d** are 65 °, 41°, and 34° by MM2, and 35°, 28°, and 27° by PM3, respectively. The two p orbitals of the double bonds are not wholly orthogonal, and the double bonds are accompanied by pyramidalization at C(2). While the average length of the standard C=C bonds is 1.32 Å, the optimized structures of **1a**, **1b**, and **1d** have double-bond lengths of 1.354, 1.355, and 1.364 Å by MM2, and 1.370, 1.378, and 1.385 Å, respectively, by PM3. As the substituent in **1** becomes larger, the angle of twisting of the p orbitals and the bond length increase. These calculations show that the substituents at C(2) cause less pyramidalization and a weaker double bond.

PM3 calculations of 2-[p-(trifluoromethyl)phenyl]adamantene (**1e**) gave a structure similar to 2-phenyladamantene (**1d**) within an angle deviation of ±1°, suggesting that the electronic factor hardly affects the twist angle of the p orbitals.

Experimental

The melting points are uncorrected. IR spectra were recorded on a Perkin Elmer 1640 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL GSX270 (270 MHz) or JEOL EX400 (400 MHz) spectrometer. In all NMR measurements TMS was used as an internal standard. ^{13}C NMR spectra were obtained with a JEOL GSX270 (67.8 MHz) or JEOL EX400 (100 MHz) spectrometer; the chemical shifts were measured relative to $CDCl_3$ and expressed with reference to TMS. The mass spectra and GC high-resolution mass spectra were recorded on a JEOL JMS-HX110 mass spectrometer. Electronic spectra were taken on a Hitachi 200-10 spectrometer. Quantitative elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto. All of 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). Lithium rods containing 1% of sodium were purchased from E. Merck Co. 3-Noradamantanecarbaldehyde (**14**) were prepared by the $LiAlH_4$ reduction of 3-noradamantanecarboxylic acid (**12**), and subsequent pyridinium chlorochromate oxidation. 1-*t*-Butyl-2-adamantanone[31] and 2-[p-(trifluoromethyl)phenyl]-2-adamantanol[32] were synthesized by a method described in the literature. The concentration of alkyllithium was determined by titration with 1-pyreneacetic acid[33] or *N*-pivaloyl-*o*-toluidine.[34] 1-Iodo-2-methyleneadamantane (**11**)[15a,15b] and 2-chloro-2-ethyl-1-iodoadamantane (**2c**)[15a,15c] were synthesized as reported previously via the acylative ring expansion of **14**. $Ba^{13}CO_3$ (98% ^{13}C) was purchased from Aldlich Chemical Co., Inc.

2-Chloro-1-iodo-2-methyladamantane (2b). Through a solution of 1-iodo-2-methyleneadamantane (**11**) (543 mg, 1.98 mmol) in CH_2Cl_2 (20 ml) at 0 °C was passed HCl gas, which was generated by the dropwise addition of concentrated aqueous HCl to concentrated H_2SO_4. After being stirred for 1 h, the solution was allowed to stand at room temperature for 1 h. Evaporation of the solvent gave colorless crystals. Recrystallization from hexane gave **2b** (527 mg, 86%) as colorless crystals: Mp 157.0—159.5 °C; IR (KBr) 2905, 1378, 1093, 1017, and 759 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.69—1.87 (6H, m), 1.97 (3H, s, CH_3), 2.07 (1H, m), 2.40 (1H, br s), 2.52—2.72 (3H, m), 2.89 (1H, m), and 3.28 (1H, m); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 32.1 (CH), 32.4 (CH), 32.5 (CH_3), 33.6 (CH_2), 33.7 (CH_2), 37.0 (CH_2), 42.6 (CH), 49.5 (CH_2), 49.6 (CH_2), 61.0 (C), and 82.1 (C). Found: C, 42.60; H, 5.04; Cl, 11.26; I, 40.68%. Calcd for $C_{11}H_{16}ClI$: C, 42.54; H, 5.19; Cl, 11.41; I, 40.86%.

(3-Noradamantyl)phenylmethanol. To a solution of PhMgBr in dry ether (15 ml), which was prepared from Mg turnings (201 mg, 8.27 mmol) and PhBr (1.23 g, 7.83 mmol), was added a solution of 3-noradamantanecarbaldehyde (**14**, 1.01 g, 6.73 mmol) in dry ether (15 ml); the mixture was refluxed under N_2 for 2 h. To the cooled mixture was added saturated NH_4Cl (15 ml). The aqueous layer was extracted with ether (3×10 ml). The combined ether layers were washed with saturated $NaHCO_3$ (25 ml) and saturated NaCl (25 ml) and dried ($MgSO_4$). Evaporation of the solvent gave pale-yellow crystals (1.59 g). Recrystallization from hexane gave (3-noradamantyl)phenylmethanol (1.16 g, 72%) as colorless crystals: Mp 88.5—92.0 °C; IR (KBr) 3347, 2921, 1453, 1024, and 712 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.19—1.37 (2H, m), 1.44—1.76 (8H, m), 2.18 (2H, br d, J = 15.4 Hz), 1.90—2.03 (2H, m), 2.42 (1H, t, J = 6.6 Hz), and 7.20—7.35 (5H, m, arom. H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 35.6 (CH_2), 37.1 (CH), 37.2 (CH), 41.2 (CH), 43.2 (CH_2), 43.9 (CH_2), 44.2 (CH_2), 46.6 (CH_2), 54.5 (C), 79.0 (CH), 126.8 (2CH), 127.1 (CH), 127.8 (2CH), and 143.0 (C). Found: C, 83.95; H, 9.13%. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83%.

3-Noradamantyl Phenyl Ketone (13d). **Method A.** To a suspension of pyridinium chlorochromate (1.49 g, 6.92 mmol) in dry CH_2Cl_2 (9.2 ml) was added a solution of (3-noradamantyl)-phenylmethanol (1.11 g, 4.61 mmol) in dry CH_2Cl_2 under a nitrogen atmosphere. After the mixture had been stirred for 3 h, ether was added and the mixture was passed through Florisil. Removal of the solvent gave a colorless oil (1.03 g). MPLC [SiO_2, hexane–ether (19 : 1)] gave **13d** as a colorless oil (973 mg, 89%), which crystallized upon chilling its solution in hexane: Mp 40.5—41.0 °C; IR (liquid film) 2927, 1664, 1279, and 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.65—1.79 (4H, m), 1.90—2.03 (4H, m), 2.21 (2H, m), 2.38 (2H, br s), 3.00 (1H, t, J = 6.7 Hz), 7.37—7.52 (3H, m, arom. H), and 7.87 (2H, m, arom. H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 35.0 (CH_2), 37.5 (2CH), 43.5 (CH), 43.8 ($2CH_2$), 48.2 ($2CH_2$), 60.7 (C), 131.6 (CH), 128.1 (2CH), 128.3 (2CH), 137.5 (C), and 205.8 (C, C=O). Found: H, 8.07; C, 84.64%. Calcd for $C_{16}H_{18}O$: H, 8.02; C, 84.91%.

Method B. A solution of PhLi in dry ether (1.1 mol dm^{-3}, 2.39 ml, 2.58 mmol) was dropwise added to a solution of 3-noradamantanecarboxylic acid (**12**, 215 mg, 1.29 mmol) in dry ether (13 ml) at 0 °C, and the mixture was stirred for 1 h. The solution was poured into saturated NH_4Cl (12 ml). The aqueous layer was extracted with ether (2×12 ml). The combined ether extracts were washed with saturated NaCl (12 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a pale-yellow oil. MPLC [SiO_2, hexane–ether (19 : 1)] gave **13d** as a colorless oil (163 mg, 56%), which crystallized upon chilling its solution in hexane.

1,2-Diiodo-2-phenyladamantane (2d). To a solution of iodine (5.72 g, 22.6 mmol) in CH_2Cl_2 (3.1 ml) was added red phosphorus (698 mg, 22.5 mmol) with stirring. The mixture was stirred at room temperature for 1.5 h and then cooled in an ice-water bath. After a solution of **13d** (425 mg, 1.88 mmol) in CH_2Cl_2 (1.5 ml) was added, the resulting mixture was stirred for 4 h in the dark. The solution was poured into ice-water (40 ml). The organic layer and dichloromethane extracts (3×1 ml) from the aqueous layer were combined, washed with saturated $NaHSO_3$ (2×40 ml), saturated $NaHCO_3$ (40 ml), and water (40 ml), and dried ($MgSO_4$). Removal of the solvent under vacuum at 0 °C gave a pale-yellow powder, which was recrystallized from hexane–CH_2Cl_2 (4 : 1) at −20 °C in the dark to afford pale yellow crystals of **2d** (487 mg, 56%): Mp 107.5—109.5 °C; IR (KBr) 2910, 1446, 1018, 950, and 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.50—2.24 (6H, m), 2.80—3.10 (4H, m), 3.16 (1H, br s), 3.51—3.65 (2H, m), 7.17—7.40 (3H, m), and 8.20 (2H, m); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 30.6 (CH_2), 32.6 (CH), 33.0 (CH), 37.1 (CH_2), 37.9 (CH_2), 45.1 (CH_2), 46.4 (CH), 57.4 (CH_2), 58.0 (C), 76.7 (C), 127.0 (2CH), 127.1 (CH), 127.4 (2CH), and 147.0 (C). Found: C, 41.30; H, 3.86; I, 54.53%. Calcd for $C_{16}H_{18}I_2$: C, 41.41; H, 3.91; I, 54.69%.

(3-Noradamantyl)[*p*-(trifluoromethyl)phenyl]methanol. To a solution of *p*-$CF_3C_6H_4MgBr$ in ether (12.0 ml), which was prepared from Mg turnings (302 mg, 12.4 mmol) and *p*-$CF_3C_6H_4Br$ (2.66 g, 11.8 mmol), was added a solution of 3-noradamantanecarbaldehyde (**14**, 1.41 g, 9.40 mmol) in dry ether (12.0 ml) over 15 min, and the mixture was refluxed for 1 h. To the cooled mixture was added saturated NH_4Cl (12.0 ml). The organic layer and ether extracts (3×10 ml) from the aqueous layer were combined, washed with saturated $NaHCO_3$ (25 ml) and saturated NaCl (25 ml), and dried ($MgSO_4$). Evaporation of the solvent gave pale-yellow crystals (2.93 g). Recrystallization from hexane gave (3-noradamantyl)-[*p*-(trifluoromethyl)phenyl]methanol (2.18 g, 78.4%) as pale yellow crystals: Mp 90.0—92.5 °C; IR (KBr) 3357, 2923, 1623, 1329, and 1136 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.18—1.32 (2H, m), 1.44—1.77 (7H, m), 1.92 (1H, m), 2.09 (1H, s), 2.20 (2H, br d, J = 13.5 Hz), 2.41 (1H, t, J = 6.6 Hz), 4.75 (1H, s), 7.43 (2H, d, J = 8.2 Hz, arom. H), and 7.56 (2H, d, J = 8.2 Hz, arom. H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 35.5 (CH_2), 37.1 (CH), 37.2 (CH), 41.3 (CH), 43.0 (CH_2), 43.9 (CH_2), 44.2 (CH_2), 46.6 (CH_2), 54.5 (C), 78.4 (CH, C–O), 124.2 (C, q, J = 271 Hz, CF_3), 124.7 (2CH, q, J = 4 Hz), 127.1 (2CH), and 129.4 (C, q, J = 32 Hz, $\underline{C}CF_3$), and 146.9 (C). Found: C, 68.78; H, 6.46%. Calcd for $C_{17}H_{19}F_3O$: C, 68.90; H, 6.46%.

3-Noradamantyl *p*-(Trifluoromethyl)phenyl Ketone (13e). To a suspension of pyridinium chlorochromate (2.27 g, 10.5 mmol) in dichloromethane (14.0 ml) was added a solution of (3-noradamantyl)[*p*-(trifluoromethyl)phenyl]methanol (2.08 g, 7.02 mmol) in CH_2Cl_2 (14.0 ml) all at once; the mixture was magnetically stirred under nitrogen at room temperature for 5 h. After ether (20 ml) was added, the solution was passed through a column of Florisil (10.0 g). The solvent was evaporated to give colorless crystals (1.98 g). Recrystallization from hexane gave **13e** as colorless crystals (1.66 g, 80%): Mp 79.5—80.5 °C; IR (KBr) 2957, 1667, 1325, 1169, 1124, and 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.61—1.80 (4H, m), 1.89—2.01 (4H, m), 2.19 (2H, m), 2.41 (2H, br s), 2.99 (1H, t, J = 6.6 Hz), 7.69 (2H, d, J = 8.2 Hz, arom. H), and 7.94 (2H, d, J = 8.2 Hz, arom. H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 35.0 (CH_2), 37.5 (2CH), 43.7 (CH), 43.9 ($2CH_2$), 48.1 ($2CH_2$), 60.9 (C), 123.7 (C, q, J = 256 Hz, CF_3), 125.2 (2CH, q, J = 4 Hz), 128.5 (2CH), 133.0 (C, q, J = 33 Hz, C–CF_3), 140.7 (C), and 205.2 (C, C=O). Found: C, 69.28; H, 5.86%. Calcd for $C_{17}H_{17}F_3O$: C, 69.38; H, 5.82%.

1,2-Diiodo-2-[*p*-(trifluoromethyl)phenyl]adamantane (2e). To a solution of iodine (4.47 g, 17.6 mmol) in CH_2Cl_2 (22.7 ml) was added red phosphorus (528 mg, 17.0 mmol) with stirring. The mixture was stirred at room temperature for 1.5 h, and then cooled in an ice-water bath. A solution of **13e** (403 mg, 1.37 mmol) in CH_2Cl_2 (1.00 ml) was added, and the resulting mixture was stirred for 4 h. The solution was poured into ice-water (40 ml). The organic layer and dichloromethane extracts (3×40 ml) from the aqueous layer were combined, washed with saturated $NaHSO_3$ (2×40 ml), saturated $NaHCO_3$ (2×40 ml), and water (40 ml), and dried ($MgSO_4$). Removal of the solvent under vacuum at 0 °C gave a pale-yellow powder (672 mg). Recrystallization from hexane at 0 °C in the dark gave **2e** (471 mg, 65%) as pale yellow crystals: Mp 175.5—177.5 °C; IR (KBr) 2910, 1614, 1323, and 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.60 (2H, s), 1.79 (1H, s), 1.87 (2H, s), 1.93 (1H, s), 2.22 (1H, m), 2.90 (1H, d, J = 12.7 Hz), 2.98—3.17 (3H, m), 3.48 (1H, m), 3.57 (1H, m), 7.57 (2H, d, J = 8.3 Hz, arom. H), and 8.33 (2H, d, J = 8.3 Hz, arom. H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 30.6 (CH_2), 32.4 (CH), 32.8 (CH), 36.9 (CH_2), 37.7(CH_2), 44.9 (CH_2), 46.0 (CH), 57.17 (CH_2), 57.21 (C), 74.2 (C), 123.8 (C, q, J = 271 Hz, CF_3), 124.5 (2CH, q, J = 4 Hz), 127.4 (2CH), 128.9 (C, q, J = 33 Hz, $\underline{C}$–CF_3), and 150.7 (C). Found: C, 38.45; H, 3.25; I, 47.56%. Calcd for $C_{17}H_{17}F_3I_2$: C, 38.37; H, 3.22; I, 47.70%.

Dehalogenation of 2-Chloro-1-iodo-2-methyladamantane (2b) with *t*-BuLi in THF. To a solution of **2b** (814 mg, 2.62 mmol) in dry THF (13 ml) cooled at −110 °C was added a solution of 1.4 mol dm^{-3} *t*-BuLi in pentane (3.74 ml, 5.24 mmol) over 5 min under nitrogen. The solution was stirred for 10 min, and then quenched with absolute methanol (5.2 ml). After most of the solvent had been removed under vacuum at room temperature, the residue was dissolved in ether. This solution was washed with saturated NaCl, saturated $NaHCO_3$, and saturated NaCl, and dried ($MgSO_4$). Evaporation of the ether afforded a colorless oil (455 mg). The oil was subjected to gas chromatography and NMR analysis, by which the product yields were determined with an error of 5%. By using preparative gas chromatography (SE-30, ϕ 2 mm×1 m) the product mixture was separated into monomeric products (150 °C) and dimeric products (300 °C). HPLC separation (μ-porasil, hexane) of the monomeric products gave 1-*t*-butyl-2-methyleneadamantane (**17b**) as a colorless oil and a mixture of 2-*t*-butyl-2-methyladamantane (**15b**) and 1-*t*-butyl-2-methyladamantane (**16b**) as a colorless oil. HPLC separation (hexane) of the dimeric products gave 2,2′-dimethylene-1,1′-biadamantane (**20**) and a mixture of 1-(2-methyl-1-adamantyl)-2-methyleneadamantane (**18b**) and 1-(2-methyl-2-adamantyl)-2-methyleneadamantane (**19**) as colorless crystals.

2-*t*-Butyl-2-methyladamantane (15b): ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.01 (s, 3H) and 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 23.4 (CH_3), 27.8 (CH), 27.9 (CH), 30.9 ($3CH_3$), 33.9 (2CH), 34.7 ($2CH_2$), 36.1 ($2CH_2$), and 41.5 (CH_2). HRMS (EI) Found: *m*/*z* 206.2019 (M^+). Calcd for $C_{15}H_{26}$: M^+, 206.2035.

1-*t*-Butyl-2-methyladamantane (16b): ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.86 (9H, s), 1.10 (3H, d, J = 7.1 Hz), 1.36 (1H, m), 1.44 (1H, m), and 1.50—1.95 (12H, m); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 20.2 (CH_3), 26.4 ($3CH_3$), 29.0 (CH), 29.2 (CH), 30.7 (CH_2), 31.5 (CH_2), 35.8 (C), 37.9 (CH_2), 38.2 (CH), 38.8 (C), 39.0 (CH_2), 39.1 (CH_2), and 41.0 (CH). HRMS (EI) Found: *m*/*z* 206.2038 (M^+). Calcd for $C_{15}H_{26}$: M^+, 206.2035.

1-*t*-Butyl-2-methyleneadamantane (17b): Colorless oil: ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.91 (3H, bs), 1.13 (6H, s), 1.63—1.85 (10H, m), 2.01 (2H, bs), 2.41 (1H, bs), 4.71 (1H, d, J = 1.6 Hz), and 4.87 (1H, d, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 24.9 ($2CH_3$), 28.2 (CH_3), 28.9 (2CH), 35.4 (C), 36.7 (CH_2), 38.0 ($2CH_2$), 39.8 ($2CH_2$), 43.8 (CH), 45.2 (C), 105.8 (CH_2), and 155.8 (C). HRMS (EI) Found: *m*/*z* 204.1882 (M^+). Calcd for $C_{15}H_{24}$: M^+, 204.1878.

1-(2-Methyl-1-adamantyl)-2-methyleneadamantane (18b): ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 20.5(CH_3), 28.9 (CH), 29.2 (CH), 29.6 (CH), 30.0 (CH), 31.4 (CH_2), 31.7 (CH_2), 37.0 (CH_2), 37.56 (CH_2), 37.63 (CH_2), 38.0 (CH_2), 38.4 (CH), 38.5 (CH_2), 39.3 (CH_2), 39.5 (CH), 40.9 (CH_2), 41.2 (C), 42.7 (CH_2), 44.9 (CH), 45.7 (C), 104.6 (CH_2), and 156.5 (C). HRMS (EI) Found: *m*/*z* 296.2511 (M^+). Calcd for $C_{22}H_{32}$: M^+, 296.2504.

1-(2-Methyl-2-adamantyl)-2-methyleneadamantane (19): ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 25.2 (CH_3), 27.1 (CH), 27.7 (CH), 28.8 (CH), 30.4 (CH), 33.2 (CH), 35.1 (CH_2), 35.3 (CH_2), 36.1 (CH_2), 36.5 (CH), 36.9 (CH_2), 37.5 (CH_2), 37.6 (CH_2), 41.0 (CH_2), 42.2 (CH_2), 43.7 (C), 44.5 (CH), 49.1 (CH_2), 51.9 (C), 107.6 (CH_2), and 157.8 (C). HRMS (EI) Found: *m*/*z* 296.2512 (M^+). Calcd for $C_{22}H_{32}$: M^+, 296.2504.

2,2′-Dimethylene-1,1′-biadamantane (20): Colorless powder; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.69—1.93 (18H, m), 2.03 (4H, m), 2.36 (2H, br d, J = 12.6 Hz), 2.45 (2H, bs), 4.79 (2H, d, J = 1.9 Hz), and 4.96 (2H, d, J = 1.9 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 28.9 (CH), 29.7 (CH), 36.3 (CH_2), 37.5 (CH_2), 38.0 (CH_2), 39.3 (CH_2), 41.2 (CH_2), 43.4 (CH), 45.0 (C), 109.3 (CH_2), and 152.8 (C). HRMS (EI) Found: *m*/*z* 294.2336 (M^+). Calcd for $C_{22}H_{30}$: M^+, 294.2348.

Dehalogenation of 2-Chloro-2-ethyl-1-iodoadamantane (2c) with *t*-BuLi in THF. To a solution of **2c** (225 mg, 0.694 mmol) in dry THF (3.5 ml) cooled at −110 °C was added a solution of 1.7 mol dm^{-3} *t*-BuLi in pentane (0.83 ml, 1.4 mmol) over 10 min under nitrogen. The solution was stirred for 20 min, and then quenched with absolute methanol (1.4 ml). After most of the solvent had been removed under vacuum at room temperature, the residue was dissolved in ether. This solution was washed with saturated NaCl, saturated $NaHCO_3$, and saturated NaCl, and dried ($MgSO_4$). Evaporation of the ether afforded a colorless oil (71 mg). The oil was subjected to NMR analysis, by which the product yields were determined with an error of 5%. MPLC separation (SiO_2, hexane) gave 1-*t*-butyl-2-ethyladamantane (**16c**) as a colorless oil and a mixture of **16c**, 1-*t*-butyl-2-ethylideneadamantane (**17c**), and 1-(2-ethyl-1-adamantyl)-2-ethylideneadamantane (**18c**). Washing the mixture with hexane gave almost pure crystals of **18c**.

1-*t*-Butyl-2-ethyladamantane (16c): Colorless oil; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.82 (3H, t, J = 7.2 Hz), 0.87 (9H, s), and 1.33—1.95 (16H, m); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 12.1 (CH_3), 22.4 (CH_2), 26.9 ($3CH_3$), 28.7 (CH), 29.1 (CH), 31.1 (CH_2), 31.7 (CH_2), 35.8 (C), 37.9 (CH_2), 39.0 (CH_2), 39.1 (C), 39.5 (CH_2), and 48.2 (CH). HRMS (EI) Found: *m*/*z* 220.2185 (M^+). Calcd for $C_{16}H_{28}$: M^+, 220.2191.

1-*t*-Butyl-2-ethylideneadamantane (17c): ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.95 (1H, br s) and 5.40 (1H, q, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.7 (CH_3), 25.2 ($3CH_3$), 28.8 (2CH), 32.2 (CH), 35.4 (C), 36.8 (CH_2), 38.2 ($2CH_2$), 38.7 ($2CH_2$), 45.0 (C), 113.6 (CH), and 146.0 (C). HRMS (EI) Found: *m*/*z* 218.2039 (M^+). Calcd for $C_{16}H_{26}$: M^+, 218.2035.

1-(2-Ethyl-1-adamantyl)-2-ethylideneadamantane (18c): Colorless crystals; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.79 (3H, t, J = 7.4 Hz), 1.35—2.07 (29H, m), 1.59 (3H, d, J = 6.3 Hz), 2.54 (1H, br d, J = 8.8 Hz), 2.98 (1H, br s), and 5.81 (1H, q, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 12.8 (CH_3), 12.4 (CH_3), 23.2 (CH_2), 28.9 (CH), 29.3 (CH), 29.5 (CH), 29.7 (CH), 30.1 (CH), 31.4 (CH_2), 32.9 (CH), 33.0 (CH_2), 36.2 (CH_2), 37.2 (CH_2), 38.0 (CH_2), 38.3 (CH_2), 38.9 (CH_2), 39.2 (CH_2), 41.1 (CH_2), 41.6 (C), 42.4 (CH_2), 45.3 (C), 46.6 (CH), 111.9 (CH), and 147.1 (C). HRMS (EI) Found: *m*/*z* 324.2808 (M^+). Calcd for $C_{24}H_{36}$: M^+, 324.2817.

Dehalogenation of 1,2-Diiodo-2-phenyladamantane (2d) with *t*-BuLi in THF. To a solution of **2d** (869 mg, 1.87 mmol) in dry THF (9.4 ml) cooled at −110 °C was added a solution of 1.56 mol dm^{-3} *t*-BuLi in pentane (3.60 ml, 5.62 mmol) over 15 min under nitrogen. The solution was stirred for 10 min, and then quenched with methanol (5.6 ml). After most of the solvent had been removed under vacuum at room temperature, the residue was dissolved in ether. This solution was washed with saturated NaCl, saturated $NaHCO_3$, and saturated NaCl, and dried ($MgSO_4$). Evaporation of the ether afforded a faintly yellow oil (482 mg). The oil was subjected to NMR analysis, by which the product yields were determined with an error of 5%. MPLC (SiO_2, hexane) afforded 2,2′-diphenyl-1,2′-biadamantane (**26**) as colorless crystals and dimer **27a** as colorless crystals as well as a mixture of 2-*t*-butyl-2-phenyladamantane (**15d**), 1-*t*-butyl-2-phenyladamantane (**16d**), and 2-phenyladamantane (**25d**)[20] as colorless crystals. Compound **15d** was isolated by recrystallization from hexane and identified by NMR data. **16d** was identified by comparing its ^{13}C chemical shifts with those of an authentic sample. The characterization of dimer **27a** is discussed in the text.

2-*t*-Butyl-2-phenyladamantane (15d): Colorless crystals; mp 85.0—86.0 °C; IR (KBr) 2875, 1473, 1364, 748, and 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.91 (9H, s), 1.42—1.50 (2H, m), 1.59—1.81 (5H, m), 1.93—2.08 (3H, m), 2.58—2.70 (4H, m), 7.07—7.14 (1H, m), and 7.19—7.29 (4H, m); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 27.0 (CH), 28.1 (CH), 31.8 ($3CH_3$), 31.9 (2CH), 34.1 ($2CH_2$), 36.5 ($2CH_2$), 38.2 (C), 40.4 (CH_2), 51.0 (C), 124.5 (CH), 126.2 (2CH), 129.6 (2CH), and 147.0 (C). Found: C, 89.24; H, 10.52%. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51%.

2,2′-Diphenyl-1,2′-biadamantane (26): Colorless crystals;

^{1}H NMR (CDCl$_3$, 270 MHz) δ = 1.14—2.10 (21H, m), 2.14 (1H, br s), 2.52—2.61 (2H, m), 2.63—2.78 (2H, m), 2.96 (1H, m), 3.19 (1H, br d, J = 12 Hz), 6.32 (1H, br d, J = 8.0 Hz), 6.50 (1H, m), 6.90 (1H, m), 7.09 (1H, m), 7.13—7.31 (5H, m), and 7.92 (1H, br d, J = 7.7 Hz); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 26.8 (CH), 28.1 (CH), 29.4 (CH), 29.6 (CH$_2$), 29.8 (CH), 32.5 (CH), 33.7 (CH), 34.2 (CH$_2$), 34.7 (CH$_2$), 36.9 (CH$_2$), 37.0 (CH$_2$), 37.8 (CH$_2$), 39.0 (CH$_2$), 39.1 (CH$_2$), 39.9 (CH), 40.3 (CH$_2$), 42.3 (CH$_2$), 46.8 (C), 54.6 (C), 56.0 (CH), 124.6 (CH), 125.0 (CH), 125.6 (CH), 126.0 (CH), 126.0 (CH), 127.6 (CH), 128.6 (CH), 129.2 (CH), 132.6 (CH), 133.8 (CH), 144.5 (C), and 148.4 (C). HRMS (EI) Found: m/z 422.2974 (M$^+$). Calcd for C$_{32}$H$_{38}$: M$^+$, 422.2975.

Dimer 27a: Colorless crystals; mp 242.0—243.5 °C; IR (KBr) 2898, 1445, and 709 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) and ^{13}C NMR (CDCl$_3$, 100 MHz) spectral data are given in Table 2. HRMS (EI) Found: m/z 420.2829 (M$^+$). Calcd for C$_{32}$H$_{36}$: M$^+$, 420.2817.

Dehalogenation of 1,2-Diiodo-2-[*p*-(trifluoromethyl)phenyl]adamantane (2e) with *t*-BuLi in THF. To a solution of **2e** (825 mg, 1.55 mmol) in dry THF (7.8 ml) cooled at −110 °C was slowly added a solution of 1.56 mol dm^{-3} *t*-BuLi in pentane (2.98 ml, 4.65 mmol) over 15 min under nitrogen. The solution was stirred for 10 min, and then quenched with methanol (4.7 ml). After most of the solvent had been removed under vacuum at room temperature, the residue was dissolved in ether. This solution was washed with saturated NaCl, saturated NaHCO$_3$, and saturated NaCl, and dried (MgSO$_4$). Evaporation of the ether afforded a faintly yellow oil (541 mg). The oil was subjected to NMR analysis, by which the product yields were determined with an error of 5%. MPLC (SiO$_2$, hexane) afforded a mixture of 2-*t*-butyl-2-[*p*-(trifluoromethyl)phenyl]adamantane (**15e**), 1-*t*-butyl-2-[*p*-(trifluoromethyl)phenyl]adamantane (**16e**), and 2-[*p*-(trifluoromethyl)phenyl]adamantane (**25e**). Compound **15e** was isolated by recrystallization from hexane and identified by NMR.

2-*t*-Butyl-2-[*p*-(trifluoromethyl)phenyl]adamantane (15e): Colorless crystals; mp 77.5—78.5 °C; IR (KBr) 2901, 1617, 1330, 1160, and 1143 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 0.90 (9H, s), 1.49 (2H, m), 1.58—1.70 (3H, m), 1.77 (2H, m), 1.87—2.01 (3H, m), 2.60—2.71 (4H, m), 7.37 (2H, d, J = 8.2 Hz, arom. H), and 7.49 (2H, d, J = 8.2 Hz, arom. H); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 26.8 (CH), 28.3 (CH), 31.7 (3CH$_3$), 31.9 (2CH), 34.0 (2CH$_2$), 36.3 (2CH$_2$), 38.1 (C), 40.2 (CH$_2$), 51.4 (C), 123.2 (2CH, q, J = 4 Hz), 124.5 (C, q, J = 271 Hz, CF$_3$), 126.8 (C, q, J = 32 Hz, $\underline{\text{C}}$–CF$_3$), 129.8 (2CH), and 151.3 (C). Found: C, 75.11; H, 8.10%. Calcd for C$_{21}$H$_{27}$F$_3$: C, 74.97; H, 8.09%.

1-*t*-Butyl-2-[*p*-(trifluoromethyl)phenyl]adamantane (16e): ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 0.69 (s, 9H, CH$_3$); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 26.3 (3CH$_3$), 28.5 (CH), 29.2 (CH), 30.3 (CH$_2$), 32.1 (CH$_2$), 36.7 (C), 37.2 (CH), 38.5 (CH$_2$), 39.9 (CH$_2$), 40.4 (CH$_2$), 41.2 (C), and 54.8 (CH). HRMS (EI) Found: m/z 336.2065 (M$^+$). Calcd for C$_{21}$H$_{27}$F$_3$: M$^+$, 336.2055.

2-[*p*-(Trifluoromethyl)phenyl]adamantane (25e). To a mixture of Me$_3$SiCl (1.04 g, 9.56 mmol),[35] NaI (1.44 g, 9.57 mmol), and acetonitrile (0.500 ml, 9.57 mmol) was added a solution of 2-[*p*-(trifluoromethyl)phenyl]-2-adamantanol[32] (472 mg, 1.95 mmol) in hexane (1.00 ml). The mixture was stirred for 24 h at room temperature, and ice-water (20 ml) was added. The organic layer and CH$_2$Cl$_2$ extracts (20 ml) from the aqueous layer were combined, washed with saturated NaHSO$_3$ (20 ml), saturated NaHCO$_3$ (20 ml), and saturated NaCl (20 ml), and dried (MgSO$_4$). Evaporation of the solvent afforded colorless crystals. MPLC (SiO$_2$, hexane) gave **25e** (305 mg, 68%) as colorless crystals: Mp 53.5—54.0 °C (from hexane); IR (KBr) 2927, 1617, 1327, and 1120 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 1.56 (1H, br s), 1.60 (1H, br s), 1.78 (5H, br s), 1.90—2.08 (5H, m), 2.49 (2H, br s), 3.03 (1H, br s), 7.46 (2H, d, J = 8.5 Hz), and 7.57 (2H, d, J = 8.5 Hz); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 27.6 (CH), 27.9 (CH), 31.0 (2CH), 31.9 (2CH$_2$), 37.7 (CH$_2$), 39.0 (2CH$_2$), 46.8 (CH), 124.4 (C, q, J = 271 Hz, CF$_3$), 125.0 (2CH, q, J = 4 Hz), 127.2 (2CH), 127.5 (C, q, J = 32 Hz, $\underline{\text{C}}$–CF$_3$), and 148.6 (C). Found: C, 72.42; H, 6.79%. Calcd for C$_{17}$H$_{19}$F$_3$: C, 72.84; H, 6.83%. HRMS (EI) Found: m/z 280.1439 (M$^+$). Calcd for C$_{17}$H$_{19}$F$_3$: M$^+$, 280.1436.

1-*t*-Butyl-2-phenyl-2-adamantanol. To a solution of 1-*t*-butyl-2-adamantanone (200 mg, 0.967 mmol)[31] in dry ether (4.83 ml) was added a solution of PhLi in ether (1.70 ml, 1.14 mol dm^{-3}, 1.94 mmol) for 15 min. After the mixture had been stirred for 3 h, water (1.70 ml) was added dropwise. The organic layer and ether extracts (2×3 ml) from the aqueous layer were combined, washed with saturated NaCl (3×3 ml), and dried (MgSO$_4$). Evaporation of the solvent gave a pale-yellow oil (305 mg). MPLC [SiO$_2$, hexane–ether (9 : 1)] gave 1-*t*-butyl-2-phenyl-2-adamantanol (257 mg, 93.3%) as colorless crystals: Mp 79.5—82.0 °C (from hexane); IR (KBr) 3440, 2909, 1597, and 1002 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 0.71 (9H, s), 1.45—1.80 (7H, m), 1.97 (1H, bs), 2.11 (1H, s, OH), 2.15 (1H, bs), 2.38 (2H, m), 2.53 (2H, m), 7.15—7.31 (3H, m, arom. H), and 7.92 (2H, d, J = 7.4 Hz, arom. H); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 28.30 (3CH$_3$), 28.32 (2CH), 33.0 (CH$_2$), 34.0 (CH$_2$), 34.5 (CH$_2$), 35.6 (CH$_2$), 37.6 (C), 39.5 (CH$_2$), 43.8 (CH), 45.8 (C), 79.5 (C, COH), 125.9 (CH), 127.2 (2CH), 128.1 (2CH), and 149.0 (C). Found: C, 84.27; H, 10.00%. Calcd for C$_{20}$H$_{28}$O: C, 84.45; H, 9.92%.

Hydrochlorination of 1-*t*-Butyl-2-phenyl-2-adamantanol. To a solution of 1-*t*-butyl-2-phenyl-2-adamantanol (82 mg, 0.29 mmol) in CH$_2$Cl$_2$ (0.6 ml) cooled at 0 °C was introduced hydrogen chloride gas over 15 min with stirring.[36] The reaction solution was subjected to gentle aspiration to remove dissolved hydrogen chloride. Evaporation of the solvent afforded a mixture of 1-*t*-butyl-2-chloro-2-phenyladamantane and 4-isopropenyl-4-methyl-3-phenylprotoadamantane as a colorless oil (50 mg). Recrystallization from hexane gave 1-*t*-butyl-2-chloro-2-phenyladamantane (13 mg, 15%) as colorless crystals.

1-*t*-Butyl-2-chloro-2-phenyladamantane: Mp 84.5—86.0 °C; ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 0.91 (9H, s), 1.45—2.23 (10H, m), 2.65 (1H, m), 2.79 (2H, m), 7.1—7.3 (3H, m), and 8.14 (2H, m); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 28.3, 28.5, 30.2 (3C), 33.5, 36.1, 37.6, 38.3, 40.0, 47.6, 89.9, 126.0, 126.3 (2C), 130.4 (2C), and 147.3.

4-Isopropenyl-4-methyl-3-phenylprotoadamantane: ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 1.36 (1H, m), 1.43 (3H, d, J = 1.1 Hz), 1.45 (3H, s), 1.53—1.77 (5H, m), 1.88—2.14 (4H, m), 2.22 (1H, m), 2.59 (1H, m), 2.77 (1H, m), 4.63 (1H, m), 4.77 (1H, br d, J = 1.4 Hz), 7.14 (1H, m), 7.26 (2H, m), and 7.47 (2H, m); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ = 22.3 (CH$_3$), 25.5 (CH$_3$), 28.6 (CH), 29.0 (CH), 32.6 (CH$_2$), 34.1 (CH$_2$), 37.3 (CH), 37.8 (CH$_2$), 38.5 (CH$_2$), 42.0 (C), 43.6 (CH$_2$), 48.7 (C), 112.6 (CH$_2$), 125.2 (CH), 127.2 (2CH), 127.8 (2CH), 150.3 (C), and 151.6 (C).

Reduction of 1-*t*-Butyl-2-chloro-2-phenyladamantane. To a solution of sodium borohydride (360 mg, 9.5 mmol) in 80% aqueous diglyme (1 ml) was added 37 mg of crude 1-*t*-butyl-2-chloro-2-phenyladamantane (37 mg, 0.12 mmol) with stirring at 50 °C.[37] The reaction mixture was stirred for 2.5 h, and cooled to room temperature. Pentane (1 ml) and solid NaOH (0.4 g) were added, and the mixture was extracted with pentane (5 ml). The extract was washed with water and dried (MgSO$_4$). Evaporation of the solvent gave a colorless oil (32 mg), which on MPLC (SiO_2, hexane) afforded a mixture of 1-*t*-butyl-2-phenyladamantane (**16d**), 4-isopropenyl-4-methyl-3-phenylprotoadamantane, and other unknown hydrocarbons with a ratio 3 : 2 : 1.

1-*t*-Butyl-2-phenyladamantane (16d): ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 26.4 (CH_3), 28.7 (CH), 29.4 (CH), 30.6 (CH_2), 32.1 (CH_2), 36.9 (C), 37.3 (CH), 38.5 (CH_2), 40.1 (CH_2), 40.4 (CH_2), 41.1(C), 54.8 (CH), 125.4 (CH), 127.7 (2CH), 128.2 (2CH), and 148.1 (C). HRMS (EI) Found: *m/z* 268.2204 (M^+). Calcd for $C_{20}H_{28}$: M^+, 268.2191.

3-Noradamantane[^{13}C]carboxylic Acid. 3-Noradamantane-[^{13}C]carboxylic acid was obtained by the reaction of 3-noradamantyllithium and [^{13}C]carbon dioxide. 3-Noradamantyllithium[16] was synthesized by the lithiation of 3-chloronoradamantane promoted by sonication.[38,39] Lithium wire (0.35 g, 51 mmol) was cut into small pieces. A mixture of 3-chloronoradamantane[40] (0.80 g, 5.1 mmol) and the lithium in hexane (29 ml) was irradiated with ultrasound (290 W) for 5 h under N_2 in a pressure bottle. The mixture was heated by an oil bath (100 °C). After the solution was cooled to -78 °C by a Dry Ice-methanol bath, $^{13}CO_2$ (generated from 98% enriched $Ba^{13}CO_3$ (2.03 g, 10.2 mmol)) was passed into the solution. After water (10 ml) was added, ether (50 ml) was added and the organic layer was extracted with 10% aqueous NaOH. The combined aqueous layer was acidified by conc. hydrochloric acid and extracted with ether (5×30 ml). The ether solution was dried ($MgSO_4$), and evaporation of the solvent gave colorless crystals (0.49 g, 58%).

[2-^{13}C]-1,2-Diiodo-2-phenyladamantane ([2-^{13}C]-2d). [2-^{13}C]-1,2-Diiodo-2-phenyladamantane (**[2-^{13}C]-2d**) was prepared from 3-noradamantane[^{13}C]carboxylic acid by a method similar to that used for synthesizing unlabeled substrates.

Calculations. Empirical molecular-mechanics calculations were performed through the MM2(87) program[19] on a FACOM M1800 computer and the MM3(92) program[27] and the MOPAC program[30] on an IBM RS/6000 computer.

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