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2,2-Divinyladamantane : A New Substrate for the Modification of Silicon Surfaces

Luc Giraud,* Vroni Huber and Titus Jenny

Université de Fribourg, Institut de Chimie Organique, Pérolles, CH-1700 Fribourg, Switzerland

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Abstract : 2,2-Divinyladamantane has been readily obtained in six steps from 2-adamantanone. The key steps were a Wittig-Horner-Emmons reaction, an ortho ester Claisen rearrangement using the microwave heating technique and a selenoxide elimination.

INTRODUCTION

The surface of silicon has been studied intensively for many years because of its paramount importance in modern technology. At the beginning of the 90's, the first textured diamond films were grown on silicon (100) substrates by microwave plasma CVD (Chemical Vapour Deposition) using a bias-enhanced nucleation process [1] and in 1993 the first oriented diamond film was deposited on silicon (100) [2]. Nucleation is increased by the presence of carbon molecules or clusters on the substrate surface which should act as seeds for the diamond nuclei, and Matsumoto [3] and Olah [4] suggested hydrocarbon cage molecules such as adamantane as possible embryos for diamond nuclei formation in the gas phase.

In 1993 Linford and Chidsey reported the first example of a densely-packed, stable organic monolayer covalently bonded directly to the silicon surface [5].

RESULTS AND DISCUSSION

Consequently, we decided to synthetise a new derivative of adamantane containing two alkene chains allowing for an oriented, bidentate connection to the silicon (111) surface (Figure) by silicon-carbon bonds [6].

* Fax ++41 (0)26 300 97 39; E-mail anne.giraud@unifr.ch

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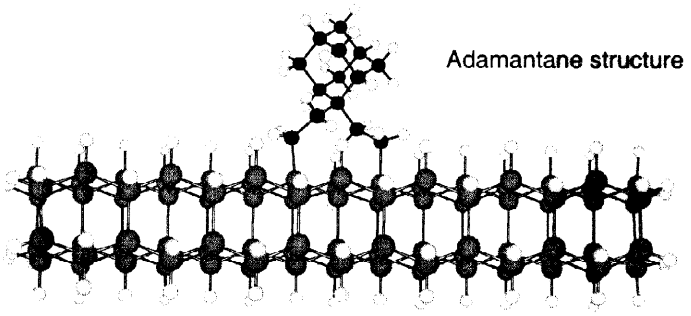
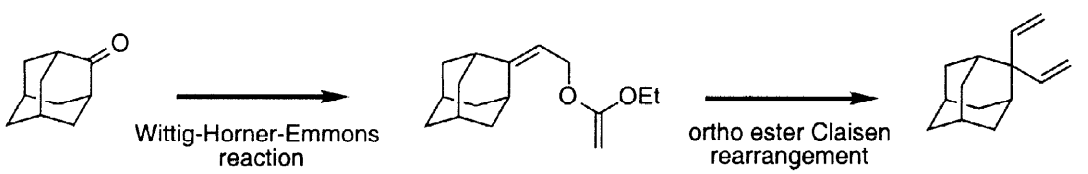
Formation of the Si-C bond from the reaction of an olefin with a silicon hydride surface may be achieved by adapting one of the known techniques, e.g. radical-mediated hydrosilylation of olefins with molecular silanes [7], photochemical hydrosilylation of olefins with trichlorosilane [8], or hydrosilylation of olefins catalyzed by transition metals complexes [9].



Figure

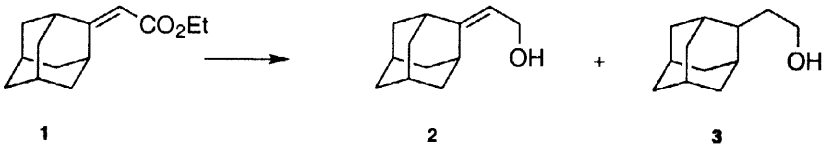
In this communication we report the synthesis of 2,2-divinyladamantane, obtained in 6 steps from adamantanone in 38% overall yield (Scheme 1), as a new substrate for the nucleation of oriented diamond growth on a silicon (111) surface. The crucial step in this synthesis is the formation of a quaternary center for which a Claisen rearrangement [10] was chosen.



Scheme 1

Thus, Wittig-Horner-Emmons reaction [11] of 2-adamantanone with triethyl phosphonoacetate using sodium hydride as base in dry THF, followed by reduction of the resultant ester **1**, with AlH_3 [12] made in situ by the addition of $LiAlH_4$ to a solution of $AlCl_3$ in THF at 0°C, furnished the allyl alcohol **2** in over 86 % yield (Scheme 3).

$LiAlH_4$ [13] in THF at room temperature and at 0°C or DIBAH [14] in CH_2Cl_2 at -80°C reduced the conjugated ester **1** to a mixture of the allylic alcohol **2** and the corresponding saturated alcohol **3** in a respective ratio of 78/22, 91/9 and 90/10 (Scheme 2).



Scheme 2

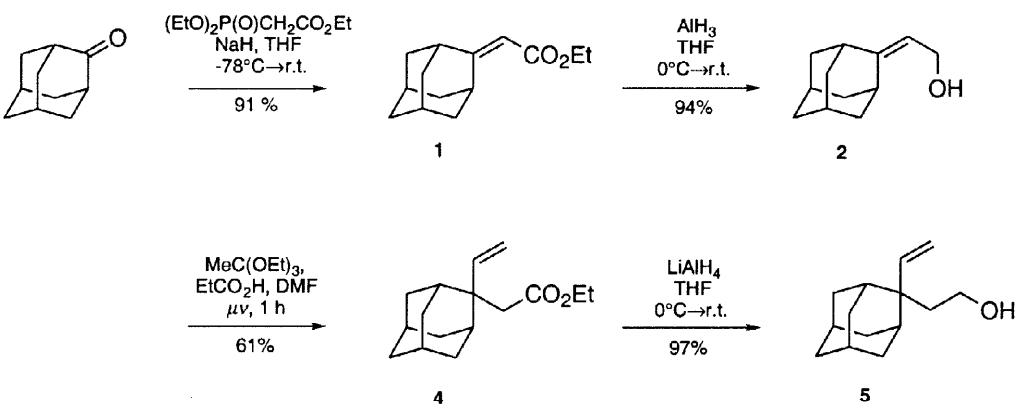
Table 1. Selectivity of the reduction of the α,β-unsaturated ester **1**.

Reductor	Solvent	Temperature	Ratio of products[a] 2 / 3	Yield (%)[b] of alcohol **2**
AlH_3	THF	r.t.	100 0	94
$LiAlH_4$	THF	r.t.	78 22	73
	THF	0 °C	91 9	77
DIBAH	CH_2Cl_2	- 80 °C	90 10	72

a) Ratio of products **2** and **3** determined by GC with a temperature program isotherm at 120 °C.

b) Yields are of isolated and purified products.

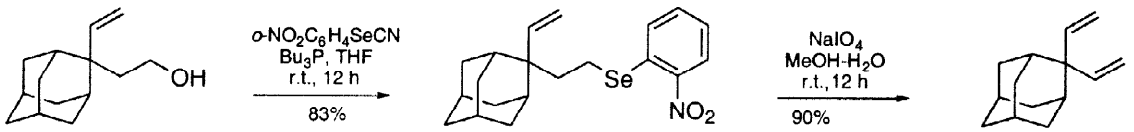
The microwave heating technique [15,16] was used for carrying out the ortho ester Claisen rearrangement (Johnson method's) [17]. Irradiation of a solution of the allylic alcohol **2**, with an excess of triethyl orthoacetate and a catalytic amount of propionic acid in dry DMF in an adapted domestic microwave oven operating at full power (650 W at 2450 MHz) furnished the γ,δ-unsaturated ester **4**. The ability to form a γ,δ-unsaturated ester as well as the ease with which a quaternary center is created in a one pot reaction are two advantages of this Claisen rearrangement. Subsequent reduction of the ester function with $LiAlH_4$ in THF gave the alcohol **5** in a yield of over 59% (Scheme 3).



Scheme 3

Although the conversion of the hydroxy ethyl side chain into the second vinyl substituent (**5** → **7**) seems to constitute a trivial synthetic operation, all our attemps to produce **7** by elimination of the corresponding mesylate either failed (using DBU) or resulted in substitution (using sodium methylate as the base). Flash pyrolysis of the corresponding acetate at 650°C only led to partial conversion. Finally treatement of the primary

alcohol **5** with *o*-nitro-phenyl selenocyanate [18,19] in THF at room temperature in the presence of tri-*n*-butylphosphine resulted in good yield (83%) of the primary alkyl selenide **6**. Oxydation of the selenide **6** with sodium metaperiodate [20,21] gave the selenoxide which eliminates seleninic acid at room temperature to give the desired olefin **7** in 90% yield (Scheme 4).



5 6 7

Scheme 4

CONCLUSION

We have presented a rapid and efficient procedure for the multigram-scale synthesis of 2,2-divinyladamantane from 2-adamantanone. The synthesis is based on the ortho ester Claisen rearrangement and the selenoxyde elimination. The hydrosilylation reaction between the silicon (111) surface, or molecular silanes and 2,2-divinyladamantane is presently being studied and the results will be presented elsewhere.

EXPERIMENTAL SECTION

THF and Et_2O were freshly distilled from Na/benzophenone under an argon atmosphere prior to use; CH_2Cl_2, DMF and benzene were distilled from CaH_2 under N_2 and toluene from Na under N_2. Solvents for chromatography were used after distillation. Flash column chromatography (FC) and filtration were performed with *Baker silica gel* (0.063-0.200 mm). TLC were run on *Merck silica gel 60 F_{254}* analytical plates; detection were carried either with UV, iodine, spraying with a solution of 25 g phosphomolybdic acid, 10 g $Ce(NH_4)_2(NO_3)_6{\cdot}4H_2O$, 60 ml conc. H_2SO_4 and 940 mL H_2O with subsequent heating, or with a solution of 3 g $KMnO_4$, 20 g K_2CO_3, 300 mL of H_2O and 5 mL of NaOH 5%, followed by heating. Melting points were determined on a *Reichert* thermovar apparatus. IR: spectra were recorded on a *Mattson Unicam 5000* spectrophotometer; in cm^{-1}. NMR: *Bruker Avance DRX-500* (^1H 500.13 MHz and ^{13}C 125.77 MHz); for ^1H δ in ppm relative to $CDCl_3$ (= 7.27 ppm), for ^{13}C δ in ppm relative to $CDCl_3$ (= 77.1 ppm), and coupling constants *J* are given in Hz. ^1H NMR splitting patterns abbreviations are: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *m*, multiplet; br., broad. ^{13}C NMR multiplicities were determined by the APT and DEPT sequences, abbreviations are: *q*, CH_3; *t*, CH_2; *d*, CH; *s*, quaternary carbons. Assignements were confirmed by NOESY, COSY and HETCOR experiments. MS: *Vacuum Generators Micromass VG 70/70E DS 11-250*; EI (70 eV); m/z (%). Elemental analysis: *Ciba specialities* Mikrolabor, Marly, Switzerland. Gas chromatographic quantitative analyses were carried out on a *Fisons HRGC MEGA 2* series gas chromatograph equipped with a *Permabond SE 54* 25 m x 0.32 mm capillary column.

Adamantan-2-ylidene-acetic acid ethyl ester (1). A solution of triethyl phosphonoacetate (22 mL, 110 mmol) in 50 mL of dry THF was added to a suspension of NaH (4.9 g, 206 mmol) in 3 mL of THF at 0 °C. The mixture was stirred at room temperature for 1 h and then cooled to -78 °C. To this was added 2-adamantanone (5 g, 33 mmol) in 15 mL THF over 10 min. The resulting mixture was stirred at -78 °C for 6 h and allowed to warm to room temperature. It was poured into 200 mL of 1:1 ether-NH_4Cl and the phases were separated. The organic layer was washed with water and the combined aqueous phases were extracted with Et_2O (3 x 100 mL). The combined extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford 16.5 g of a yellow oil. Flash chromatography on silica gel with hexane/AcOEt (98 : 2) afforded 6.7 g (91%) of **1** as a colorless liquid. ^1H NMR ($CDCl_3$): δ = 5.58 (*s*, 1H, C*H*=), 4.13 (*q*, *J* = 7.1, 2H, OCH_2CH_3), 4.05 (br.*s*, 1H, C(3)-*H*), 2.43 (br.*s*, 1H, C(1)-*H*), 1.96 (br.*s*, 2H, C(5)-*H*, C(7)-*H*), 1.96-1.92 (*m*, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.86 (br.*s*, C(6)H_2), 1.86-1.81 (*m*, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}), 1.27 (t, *J* = 7.1, 3H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ = 171.6 (*s*, CO_2), 166.5 (*s*, C(2)), 108.5 (*d*, CH=), 58.9 (*t*, OCH_2), 41.1 (*d*, C(1)), 39.9 (*t*, C(8), C(9)), 38.9 (*t*, C(4), C(10)), 36.6 (*t*, C(6)), 32.5 (*d*, C(3)), 27.7 (*d*, C(5), C(7)), 14.0 (*q*, CH_3). EI-MS: m/z (%) = 220 (76, M^+), 191 (17), 174 (100), 146 (43), 105 (72), 91 (86), 77 (75). Anal. Calcd for $C_{14}H_{20}O_2$ (220.31) : C, 76.33; H, 9.15. Found : C, 77.03; H, 9.39.

Adamantan-2-ylidene-ethanol (2). To a stirred suspension of AlH_3, made *in situ* by the addition of $LiAlH_4$ (6.2 g, 164 mmol) to a solution of $AlCl_3$ (7.3 g, 55 mmol) in THF (40 mL) under N_2 in an ice bath, was added a solution of ester **1** (6.0 g, 27 mmol) in THF (20 mL) with a syringe within ca. 30 min. Stirring was continued for 3 h at 0 °C before the mixture was allowed to warm up to r.t. After addition of MeOH (3 mL), the precipitate formed was filtered. The aqueous layer was extracted with Et_2O (3 x 100 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by flash chromatography (hexane/Et_2O 1 : 1) to yield 6.10 g (94%) of alcohol **2**. ^1H NMR ($CDCl_3$): δ = 5.21 (*d*, *J* = 7.0, 1H, C*H*=), 4.02 (*t*, *J* = 7.0, 2H, CH_2OH), 3.18 (br.*s*, 1H, *OH*), 2.77 (br.*s*, 1H, C(3)-*H*), 2.28 (br.*s*, 1H, C(1)-*H*), 1.96 (br.*s*, 2H, C(5)-*H*, C(7)-*H*), 1.91 (br.*d*, *J* = 11.6, 2H, C(4)-H_{syn}, C(10)-H_{syn}), 1.88 (br.*d*, *J* = 13.1, 2H, C(8)-H_{syn}, C(9)-H_{syn}), 1.79 (br.*d*, *J* = 13.1, 2H, C(8)-H_{anti}, C(9)-H_{anti}), 1.72 (br.*d*, *J* = 11.6, 2H, C(4)-H_{anti}, C(10)-H_{anti}). ^{13}C NMR ($CDCl_3$): δ = 151.3 (*s*, C(2)), 115.6 (*d*, CH=), 57.5 (*t*, OCH_2), 40.12 (*d*, C(1)), 39.5 (*t*, C(8), C(9)), 38.8 (*t*, C(4), C(10)), 36.9 (*t*, C(6)), 32.2 (*d*, C(3)), 28.3 (*d*, C(5), C(7)). EI-MS: m/z (%) = 178 (25, M^+), 149 (38), 135 (82), 105 (35), 91 (80), 79 (100), 55 (39). Anal. Calcd for $C_{12}H_{18}O$ (178.27) : C, 80.85; H, 10.18; Found : C, 80.63; H, 10.11.

Adamantan-2-ethanol (3). To a stirred suspension of $LiAlH_4$ (1.14 g, 30.0 mmol) in THF (10 mL) under N_2 in a ice bath, was introduced a solution of ester **1** (6 g, 27.2 mmol) in THF (10 mL) with a syringe within ca. 30 min. The mixture was stirred for further 3 h at 0 °C and allowed to warm up to r.t. After addition of MeOH (2 mL), the precipitate formed was filtered. The aqueous layer was extracted with Et_2O (3 x 100 mL), dried over $MgSO_4$ and evaporated *in vacuo*. Purification by flash chromatography (hexane/Et_2O 1 : 1) gave 3.7 g (77%) of alcohol **2** and 0.4 g (8%) of alcohol **3**. ^1H NMR ($CDCl_3$): δ = 3.53 (*t*, *J* = 6.9, 2H, CH_2O), 3.16 (br.*s*, 1H, *OH*), 2.44 (br.*s*, 1H, C(1)-*H*), 1.90 (br.*d*, *J* = 11.5, 2H, C(8)-H_{syn}, C(9)-H_{syn}), 1.86 (br.*s*, 1H, C(5)-*H*), 1.85 (br.*d*, *J* = 13.0, 2H, C(4)-H_{syn}, C(10)-H_{syn}), 1.82 (*m*, 1H, C(2)-*H*), 1.79 (br.*s*, 1H, C(7)-*H*), 1.73 (br.*d*, *J* = 11.5, 2H, C(8)-H_{anti}, C(9)-H_{anti}), 1.72 (br.*s*, 2H, C(6)H_2), 1.71 (*m*, CH_2CH_2O), 1.67 (br.*s*, 1H, C(3)-*H*), 1.52 (br.*d*, *J* = 13.0, 2H, C(4)-H_{anti}, C(10)-H_{anti}). ^{13}C NMR ($CDCl_3$): δ = 60.1 (*t*,

CH_2OH), 40.5 (*d*, C(1)), 38.9 (*t*, C(8), C(9)), 38.2 (*t*, CH_2CH_2O), 35.5 (*t*, C(6)), 31.8 (*d*, C(3)), 31.5 (*t*, C(4), C(10)), 28.1 (*d*, C(5)), 28.0 (*d*, C(2)), 27.9 (*d*, C(7)). EI-MS: m/z (%) = 180 (14, M^+), 162 (55), 149 (11), 135 (92), 105 (32), 91 (86), 79 (100), 55 (22). Anal. Calcd for $C_{12}H_{20}O$ (180.29) : C, 79.94; H ,11.18; Found : C, 80.11; H, 11.19.

(2-Vinyl-adamantan-2-yl)-acetic acid ethyl ester (4). A solution of allylic alcohol **2** (1.5 g, 8.4 mmol), triethyl orthoacetate (10.8 mL, 59 mmol) and propionic acid (0.03 mL, 0.4 mmol) in dry DMF (20 mL) in an Erlenmeyer flask (500 mL capacity without any boiling chips) was placed in an adapted domestic microwave oven (650W, 2450 MHz) and irradiated for 1 h at full power. After the irradiation, the mixture was cooled, diluted in Et_2O (100 mL), washed with 0.5 N HCl and brine, and dried over $MgSO_4$. Evaporation of the solvent and purification by flash chromatography (hexane/Et_2O 19 : 1) afforded 1.3 g (61 %) of ester **4**. ^1H NMR ($CDCl_3$): δ = 5.80 (*dd*, *J* = 18.0, 11.1, 1H, C*H*=CH_2), 5.17 (*dd*, *J* = 11.1, 1.3, 1H, CH_2=CH, *cis*), 4.98 (*dd*, *J* = 18.0, 1.2, 1H, CH_2=CH, *trans*), 4.06 (*q*, *J* = 7.2, 2H, OCH_2), 2.59 (*s*, 2H, CH_2CO_2), 2.08 (br.*d*, *J* = 10.2, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.06 (br.*d*, *J* = 11.4, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.97 (br.*s*, 2H, C(1)-*H*, C(3)-*H*), 1.87 (*m*, 1H, C(7)-*H*), 1.79 (m, 1H, C(5)-*H*), 1.68 (br.*s*, 2H, C(6)H_2), 1.67 (br.*d*, *J* = 10.2, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.55 (br.*d*, *J* = 11.4, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 1.22 (*t*, *J* = 7.1, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 172.1 (*s*, CO_2), 145.5 (*d*, *C*H=CH_2), 113.6 (*t*, *C*H_2=CH), 59.8 (*t*, OCH_2), 44.3 (*s*, C(2)), 43.6 (*t*, *C*H_2CO_2), 38.9 (*t*, C(6)), 34.3 (*d*, C(1), C(3)), 33.6 (*t*, C(4), C(9)), 32.7 (*t*, C(8), C(10)), 27.9 (*d*, C(7)), 27.7 (*d*, C(5)), 14.3 (*q*, *C*H_3). EI-MS: m/z (%) = 248 (51, M^+), 202 (31), 174 (67), 161 (100), 133 (43), 119 (57), 105 (51), 91 (93), 79 (98). Anal. Calcd for $C_{16}H_{24}O_2$ (248.36) : C, 77.38; H, 9.74; Found : C, 77.41; H, 9.80.

(2-Vinyl-adamantan-2-yl)-ethanol (5). To a stirred mixture of $LiAlH_4$ (0.38 g, 10.0 mmol) in dry THF (10 mL) under argon at 0 °C was added a solution of ester **4** (2.21 g, 8.90 mmol) in dry THF (10 mL) over 30 min. The mixture was stirred at 0 °C for 1 h, allowed to warm to room temperature for 2 h, cooled to 0 °C (ice bath), quenched with 5 mL of water and then treated with 150 mL of saturated aqueous Rochelle's salt. The reaction mixture was extracted with Et_2O (3 x 100 mL). The combined extracts were dried over $MgSO_4$ and concentrated under reduced pressure to afford 1.82 g of a colorless liquid. Flash chromatography (hexane/Et_2O 1 : 1) and recrystallisation from hexane gave 1.78 g (97%) of compound **5**.
White solid. M.p. 40-41 °C. ^1H NMR ($CDCl_3$): δ = 5.69 (*dd*, *J* = 18.1, 11.1, 1H, C*H*=CH_2), 5.17 (*dd*, *J* = 11.2, 1.5, 1H, CH_2=CH *cis*), 4.95 (*dd*, *J* = 18.0, 1.5, 1H, CH_2=CH *trans*), 3.60 (*t*, *J* = 7.6, 2H, CH_2OH), 2.37 (*s*, 1H, *OH*), 2.12 (br.*d*, *J* = 12.9, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.04 (br.*d*, *J* = 12.4, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.86 (*m*, 1H, C(7)-*H*), 1.85 (*t*, *J* = 7.6, 2H, CH_2CH_2O), 1.79 (*m*, C(5)-*H*), 1.72 (br.*s*, 2H, C(1)-*H*, C(3)-*H*), 1.67 (br.*s*, 2H, C(6)H_2), 1.62 (br.*d*, *J* = 12.9, 2H, C(8)-H_{anti}, C(10)-H_{anti}), 1.52 (br.*d*, *J* = 12.4, 2H, C(4)-H_{anti}, C(9)-H_{anti}). ^{13}C NMR ($CDCl_3$): δ = 147.2 (*d*, *C*H=CH_2), 113.0 (*t*,*C*H_2=CH), 58.8 (*t*, *C*H_2OH), 43.6 (*s*, C(2)), 40.0 (*t*, *C*H_2CH_2O), 38.9 (*t*, C(6)), 34.3 (*d*, C(1), C(3)), 33.5 (*t*, C(4), C(9)), 32.5 (*t*, C(8), C(10)), 28.2 (*d*, C(5)), 27.7 (*d*, C(7)). EI-MS: m/z (%) = 206 (5, M^+), 188 (78), 175 (43), 161 (85), 145 (18), 133 (42), 119 (49), 105 (54), 91 (89), 79 (100), 67 (47). Anal. Calcd for $C_{14}H_{22}O$ (206.33) : C, 81.50; H, 10.75; Found : C, 81.41; H, 10.80.

2-[2-(2-Nitro-phenylselanyl)-ethyl]-2-vinyl adamantane (6). A solution of alcohol **5** (1.28 g, 6.20 mmol) in THF (30 mL) containing *o*-nitrophenyl selenocyanate (1.70 g, 7.49 mmol) under nitrogen

atmosphere was treated dropwise with tri-*n*-butylphosphine (1.5 g, 7.41 mmol) at room temperature. After stirring the reaction mixture for 12 h, the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (150 mL) , washed with water (200 mL), dried over $MgSO_4$ and concentrated under reduce pressure to afford 5.18 g of a yellow oil. Flash chromatography (hexane/Et_2O 95 : 5) and recristallisation from hexane gave 2.01 g (83%) of compound **6**. Yellow solid. M.p. 74.5-75.5 °C. ^1H NMR ($CDCl_3$): δ = 8.28 (*m*, 1 arom. H, *ortho* to NO_2), 7.50 (*m*, 1 arom. H, *para* to NO_2), 7.49 (*m*, 1 arom. H, *ortho* to Se), 7.29 (*m*, 1 arom. H, *para* to Se), 5.72 (*dd*, *J* = 18.1, 11.2, 1H, C*H*=CH_2), 5.33 (*dd*, *J* = 11.2, 1.3, 1H, CH_2=CH, *cis*), 5.05 (*dd*, *J* = 18.1, 1.3, 1H, CH_2=CH, *trans*), 2.81 (*m*, 2H, CH_2Se), 2.06 (br.*d*, *J* = 11.9, 2H, C(8)-H_{syn}, C(10)-H_{syn}), 2.05 (br.*d*, *J* = 13.7, 2H, C(4)-H_{syn}, C(9)-H_{syn}), 1.95 (*m*, 2H, CH_2CH_2Se), 1.88 (*m*, 1H, C(5)-*H*), 1.83 (*m*, 2H, C(7)-*H*), 1.78 (br.*s*, 2H, C(1)-*H*, C(3)-*H*), 1.68 (br.*s*, 2H, C(6)H_2), 1.64 (br.*d*, *J* = 13.7, 2H, C(4)-H_{anti}, C(9)-H_{anti}), 1.56 (br.*d*, *J* = 11.9, 2H, C(8)-H_{anti}, C(10)-H_{anti}). ^{13}C NMR ($CDCl_3$): δ = 146.8 (*s*, *C*-NO_2), 146.2 (*d*, *C*H=CH_2), 133.9 (*s*, *C*-Se), 133.4 (*d*, =*C*H, *para* to NO_2), 129.1 (*d*, =*C*H, *ortho* to Se), 126.4 (*d*, =*C*H, *ortho* to NO_2), 125.2 (*d*, =*C*H, *para* to Se), 114.0 (*t*, *C*H_2=CH), 45.6 (*s*, C(2)), 38.7 (*t*, C(6)), 35.5 (*t*, *C*H_2CH_2Se), 33.8 (*d*, C(1), C(3)), 33.6 (*t*, C(8), C(10)), 32.4 (*t*, C(4), C(9)), 28.2 (*d*, C(5)), 27.6 (*d*, C(7)), 20.3 (*t*, *C*H_2Se). EI-MS: m/z (%) = 390 (5, M^+), 345 (15), 269 (17), 202 (61), 161 (100), 133 (28), 119 (43), 106 (52), 91 (92), 79 (81), 67 (66). Anal. Calcd for $C_{20}H_{25}NO_2Se$ (390.38) : C, 61.63; H, 6.45; N, 3.59; Found : C, 61.66; H, 6.54; N, 3.50.

2,2-Divinyl adamantane (7). To a solution of sodium periodate (2.64 g, 12.34 mmol) dissolved in aqueous methanol (MeOH/H_2O 7 : 3, 10 mL) was added slowly a solution of seleno ether **6** (2.41 g, 6.17 mmol) in 20 mL of THF. The reaction mixture was stirred for 12 h at room temperature, poured into a cold aqueous solution of NH_4Cl (50 mL), and extracted with AcOEt (3 x 100 mL). The organic layer was washed with 1 N HCl, $NaHCO_3$, dried over $MgSO_4$ and concentrated under reduce pressure. Flash chromatography (hexane) gave 1.05 g (90%) of compound **7** as a colorless liquid. ^1H NMR ($CDCl_3$): δ = 5.74 (*dd*, *J* = 17.9, 10.9, 2H, C*H*=CH_2), 5.10 (*dd*, *J* = 10.9, 1.4, 2H, CH_2=CH, *cis*), 4.98 (*dd*, *J* = 17.9, 1.4, 2H, CH_2=CH, *trans*), 2.13 (br.*d*, *J* = 13.0, 4H, C(4)-H_{syn}, C(8)-H_{syn}, C(9)-H_{syn}, C(10)-H_{syn}), 1.98 (br.*s*, 2H, C(1)-*H*, C(3)-*H*), 1.86 (br.*s*, 2H, C(5)-*H*, C(7)-*H*), 1.70 (br.*s*, 2H, C(6)H_2), 1.62 (br.*d*, *J* = 13.0, 4H, C(4)-H_{anti}, C(8)-H_{anti}, C(9)-H_{anti}, C(10)-H_{anti}). ^{13}C NMR ($CDCl_3$): δ = 146.2 (*d*, *C*H=CH_2), 111.8 (*t*, *C*H_2=CH), 48.3 (*s*, C(2)), 38.4 (*t*, C(6)), 34.3 (*d*, C(1), C(3)), 33.2 (*t*, C(4), C(8), C(9), C(10)), 28.1 (*d*, C(5), C(7)). EI-MS: m/z (%) = 188 (43, M^+), 159 (16), 131 (86), 117 (31), 105 (42), 91 (81), 79 (100), 67 (34), 53 (30). Anal. Calcd for $C_{14}H_{20}$ (188.31) : C, 89.30; H, 10.70; Found : C, 89.23; H, 10.75.

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REFERENCES

1. Yugo, S.; Kanai, T.; Kimura, T.; Muto, T. *Appl. Phys. Lett.* **1991**, *58*, 1036.
2. Jiang, X.; Klages, C. P. *Diamond Relat. Mater.* **1993**, *2*, 1112.
3. Matsumoto, S.; Matsui, Y. *Mater. Sci.* **1983**, *18*, 1783.
4. Olah, G. A. In *Cage Hydrocarbons* ; Olah, G. A.; Von Schleyer, P. Eds.; John Wiley and Sons, New York, 1990; pp. 1-45.
5. Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117*, 3145.
6. Giraud, L.; Jenny, T.; Küttel, O. M.; Leroy, E.; Schlapbach, L. *Appl. Phys. Lett.* **1998**, accepted.
7. Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994.
8. Bevan, W. I.; Haszeldine, R. N.; Middleton, J.; Tipping, A. E. *J. Chem. Soc. Perkin I* **1974**, 2305.
9. Speier, J. L. In *Advances in Organometallic Chemistry* ; Stones, F. G. A.; West, R. Eds.; Academic Press, New York, 1979; pp. 407-447.
10. Claisen, L. *Ber.* **1912**, *45*, 3157.
11. Narayanan, V. L.; Setescak, L. *J. Org. Chem.* **1971**, *36*, 4127.
12. Ikeda, T.; Yue, S.; Hutchinson, C. R. *J. Org. Chem.* **1985**, *50*, 5193.
13. Knier, B. L.; Rodriguez, C. L. *Tetrahedron Lett.* **1985**, *26*, 2183.
14. DeNinno, M. P.; Danishefsky, S. J.; Schulte, G. *J. Am. Chem. Soc.* **1988**, *110*, 3925.
15. Abramovitch, R. A. *Org. Prep. Proc. Int.* **1991**, *23*, 683.
16. Srikrishna, A.; Nagaraju, S.; Kondaiah, P. *Tetrahedron* **1995**, *51*, 1809.
17. Johnson, W. S.; Werthemnann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T. T.; Faulkner, D. J.; petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.
18. Grieco, P. A.; Hiroi, K.; Reap, J. J.; Noguez, J. A. *J. Org. Chem.* **1975**, *40*, 1450.
19. Grieco, P. A.; Masaki, Y.; Boxler, D. *J. Am. Chem. Soc.* **1975**, *97*, 1597.
20. Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137.
21. Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.