

Synthesis of Novel Carbo- and Hetero-polycycles. Part 8.¹ An Efficient and Convenient Synthesis of Adamantylidenevinylidenecyclopropane Derivatives

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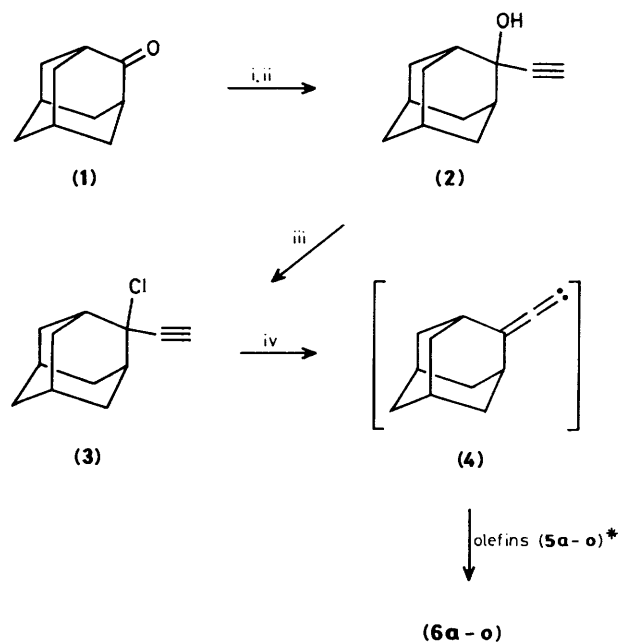
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Crown ether catalysed dehydrochlorination of 2-chloro-2-ethynyladamantane (**3**) with Bu^tOK provided a convenient and efficient method for the synthesis of adamantylidenevinylidene (**4**). In the presence of olefins (**5a—o**), compound (**4**) afforded the corresponding adamantylidenevinylidenecyclopropane derivatives (**6a—o**) in 30—81% yields.

Unsaturated carbenes such as alkylidene- and vinylidene-carbenes have attracted interest from synthetic as well as theoretical chemists in recent years.² We and others have previously reported a convenient and efficient method for the generation of dialkylidene- and dialkylvinylidene-carbenes *via* phase-transfer catalysed dehydrohalogenation of the appropriate vinyl bromide,³ and prop-2-ynyl and allenyl halides.⁴ Although the fluoride-initiated elimination route of some halogenosilyl precursors has also been developed recently, both for alkylidene-⁵ and vinylidene-carbenes⁶ under neutral conditions, the cyclopropanations of olefinic substrates stable to alkali can be carried out more economically and conveniently by the phase-transfer catalysed generation of the unsaturated carbenes from readily available corresponding halides. We report in this paper an efficient and convenient synthesis of adamantylidenevinylidenecyclopropane derivatives using the phase-transfer catalysed dehydrochlorination of 2-chloro-2-ethynyladamantane (**3**) in the presence of olefinic substrates (**5a—o**).

Results and Discussion

As the precursor of adamantylidenevinylidene (**4**), we employed 2-chloro-2-ethynyladamantane (**3**) because of its ready availability from the corresponding alcohol (**2**) (Scheme 1). Although both compounds (**2**) and (**3**) are known,⁷ we prepared (**2**) by a modified procedure using commercially available sodium acetylide suspension in xylene[†] instead of by *in situ* generation in liquid ammonia.⁷ In order to compare the catalytic effect of crown ethers with quaternary ammonium salts, adamantylidenevinylidenecyclopropanation of styrene (**5a**) was examined under several conditions by using 18-crown-6 and benzyltriethylammonium chloride (BTAC) as popular and previously evaluated phase-transfer catalysts. The reaction was carried out by slow addition of the chloride (**3**) in benzene to a vigorously stirred mixture of alkali (51% aqueous KOH or Bu^tOK), benzene, and styrene (**5a**) in the presence or absence of the catalyst. The results are summarized in Table 1. Under the two-phase reaction conditions using a large excess of 51% aqueous KOH as the base, both BTAC and 18-crown-6 gave comparable yields (61.0 and 62.3%) of the cycloadduct (**6a**) (entries 1 and 2). However, among the reactions using Bu^tOK as the base, 18-crown-6 gave a better yield (80.6%) of (**6a**) than BTAC (59.4%) (entries 3 and 4). The catalytic effect of 18-crown-6 and BTAC is apparent from the results of entries 5 and 6. Therefore, the adamantylidenevinylidenecyclopropanation of



Scheme 1. Reagents: i, NaC≡CH/xylene-THF; ii, H₂SO₄; iii, Conc. HCl-CaCl₂; iv, Base/phase-transfer catalyst; * see Table 2

the olefinic substrates (**5b—o**) was conducted under the conditions of entry 4 in Table 1. The results are summarized in Table 2.

All of the reactions afforded the corresponding cycloadducts (**6b—o**) in moderate to good yields. The products were isolated by preparative t.l.c. (silica gel or alumina) as crystals. The structures of (**6a—o**) were confirmed by spectral and analytical data (Table 3).

A characteristic feature of the products is the appearance of the allenic band at 2 000—2 020 cm⁻¹ in the i.r. spectra and a broad singlet at δ 2.60—2.45 (2 H) due to the allylic bridgehead protons of adamantane ring in the ¹H n.m.r. spectra.

The *E*-stereochemistry of (**6b**) is supported by the coupling constant *J* 4.5 Hz of the δ 2.57 signal due to the benzylic cyclopropane ring proton. The *exo*-stereochemistry of (**6d**) and (**6e**) was supported by the appearance of characteristic AB quartet signals at δ 1.18 and 0.91, respectively. The reaction with isoprene (**5h**) afforded a 5:1 mixture of regioisomers (**6h**) and (**6h'**) (¹H n.m.r. analysis, Table 3) but their separation was not successful. The monoterpene olefins (**5i—k**) gave the corresponding cycloadducts (**6i—k**) respectively. Their stereo-

[†] Fluka catalogue, 1986/87, 71205; Aldrich catalogue, 1986/87, 24957-2.

Table 1. Adamantylidenevinylidenecyclopropanation of styrene (**5a**) under various conditions^a

Entry	Base (mol)	Catalyst ^b	Reaction time (h) ^f	Yield (%) of (6a) ^g
1	aq. 51% KOH (excess)	BTAC ^c	38.5	61.0
2	aq. 51% KOH (excess)	18-C-6 ^d	62.0	62.3
3	Bu ^t OK (2.0)	BTAC ^c	48.0	59.4
4	Bu ^t OK (2.0)	18-C-6 ^d	24.0	80.6
5	Bu ^t OK (2.0)	None	68.5	Trace
6	Bu ^t OK (2.0)	None ^e	15.5	Trace

^a All reactions were carried out using 3 mol equiv. of (**5a**) at room temperature (20–28 °C) under argon in vigorously stirred benzene (see Experimental section). ^b 20 mol% Used. ^c Benzyltriethylammonium chloride. ^d 18-Crown-6-ether. ^e Under ultrasonic irradiation. ^f The addition time (ca. 1.5 h) of (**3**) in benzene was included. ^g Isolated yield of (**6a**) after preparative t.l.c.

Table 2. Adamantylidenevinylidenecyclopropanation of a variety of olefins (**5a**–**o**)^a

Olefin	Reaction time (h) ^b	Product	Yield (%) ^c	M.p. (°C)
Styrene (5a) ^d	24.0	(6a)	80.6	80–82
(<i>E</i>)-β-Methylstyrene (5b)	71.0	(6b)	30.0	55–56
α-Methylstyrene (5c)	18.5	(6c)	57.8	54–55
Norbornadiene (5d)	68.0	(6d)	77.8	103–105
Norbornene (5e)	90.0	(6e)	69.4	175–176
2,3-Dimethylbuta-1,3-diene (5f)	7.0	(6f)	74.5	35–36
2,5-Dimethylhexa-2,4-diene (5g)	67.0	(6g)	74.5	69–71
Isoprene (5h)	18.5	(6h) + (6h') ^e	70.5	40–42
α-Pinene (5i)	39.0	(6i)	52.6	71–72
β-Pinene (5j)	47.5	(6j)	37.9	122–123
Camphene (5k)	48.0	(6k)	57.5	129–131
3,4-Dihydro-2 <i>H</i> -pyran (5l)	38.0	(6l)	75.5	53–55
Ethyl vinyl ether (5m)	24.0	(6m)	77.8	67–69
1-Methoxycyclohexa-1,4-diene (5n)	25.0	(6n)	68.2	62–64
3-Methylbut-2-en-1-ol (5o)	22.5	(6o)	39.8	115–117

^a All reactions were carried out at room temperature (20–28 °C) in vigorously stirred benzene using olefin (10 mol equiv. unless otherwise noted), Bu^tOK (2 mol equiv.), 18-crown-6 ether (20 mol %), and (**3**) (1 mol equiv.) under argon. The products were isolated by preparative t.l.c. (silica gel–hexane unless otherwise noted) (see Experimental section). ^b The addition time (ca. 1.5 h) of (**3**) was included. ^c Isolated yield. ^d A 3 mol equiv. amount was used. ^e A 5:1 mixture of (**6h**) and (**6h'**).

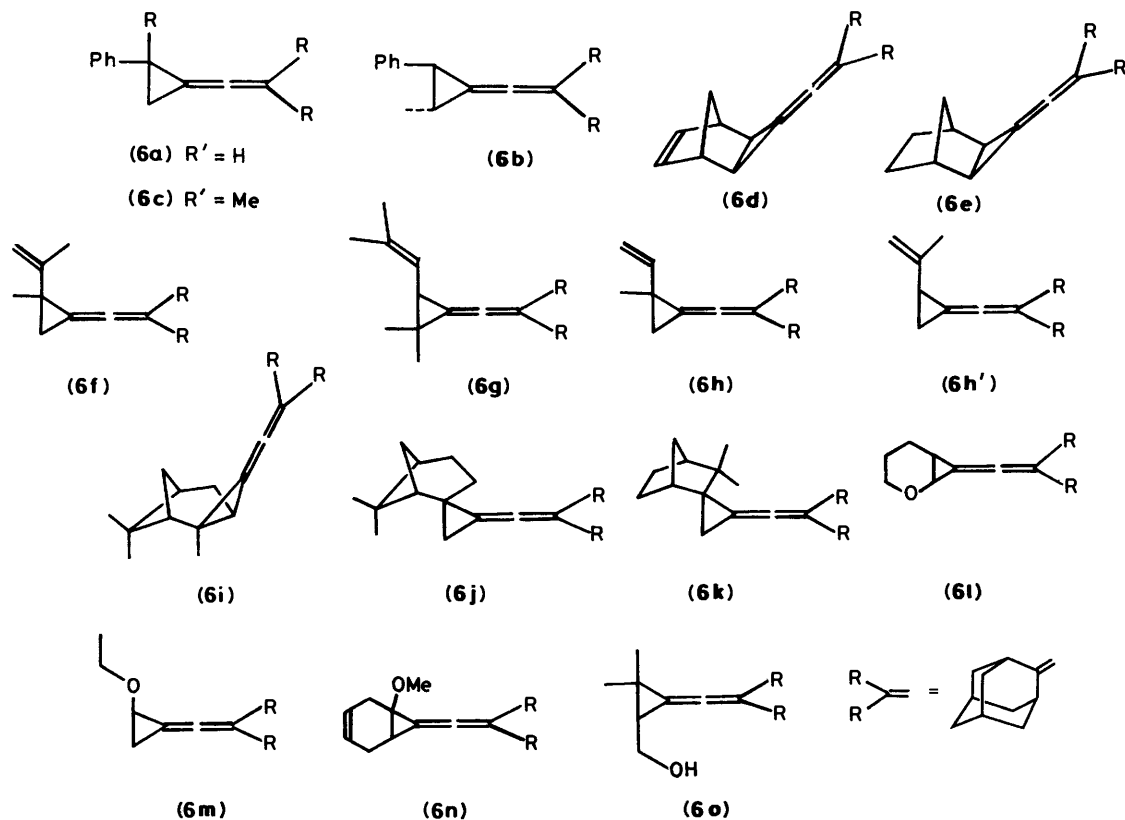


Table 3. Spectral and analytical data of adamantylidenevinylidenecyclopropane derivatives (6a—o)

Compd.	ν_{\max} (cm ⁻¹) ^a	δ_{H} ^b	m/z (%)	Formula	Required (Found)	
					C	H
(6a)	3 030, 2 920, 2 850, 2 020, 1 600, 1 500, 1 450, 750, and 690	7.19 (s, 5 H), 2.81 (dd, J 5.3 and 3.8, 1 H), 2.50 (br s, 2 H), 2.30—1.75 (m, 15 H), 1.45 (dd, J 5.3 and 6.0, 1 H) ^c	262 (37), ^d 205 (15), 141 (18), 128 (25), 115 (22), 91 (64), 79 (42), 77 (37), 51 (42), 49 (93), and 41 (100)	C ₂₀ H ₂₂	91.55 (91.35)	8.45 (8.65)
(6b)	3 010, 2 920, 2 830, 2 010, 1 600, 1 490, 1 440, 740, and 690	7.20—7.15 (m, 5 H), 2.58 (br s, 2 H), 2.57 (d, J 4.5, 1 H), 1.93—1.64 (m, 13 H), and 1.34 (d, J 5.5, 3 H)	278 (1.7), 277 (9.0), 276 (35), ^d 275 (8.0), 261 (31), 155 (31), 141 (42), 91 (100), 77 (57), 67 (52), 67 (52), 55 (53), and 51 (52)	C ₂₁ H ₂₄	91.25 (91.1)	8.75 (8.9)
(6c)	3 000, 2 960, 2 900, 2 840, 2 000, 1 600, 1 580, 1 440, 1 060, 750, and 680	7.38—7.03 (m, 5 H), 2.60 (br s, 2 H), 2.05—1.75 (m, 12 H), 1.65 (s, 2 H), and 1.60 (s, 3 H) ^c	278 (2.0), 277 (16), 276 (68), ^d 275 (9.2), 261 (17), 141 (52), 115 (38), 105 (46), 91 (100), 79 (86), and 77 (96)	C ₂₁ H ₂₄	91.25 (91.25)	8.75 (8.75)
(6d) ^h	2 920, 2 840, 2 000, 1 450, 1 340, 1 310, 1 090, 1 060, 700, and 660	6.29 (t, J 1.6, 2 H), 3.00 (br s, 2 H), 2.53 (br s, 2 H), 2.30—1.68 (m, 14 H), and 1.18 (ABq, J 9.0, $J/\Delta\delta = 0.375$, 2 H)	252 (1.4), 251 (9.0), 250 (40), ^d 249 (8.4), 135 (43), 129 (73), 115 (64), 91 (100), 81 (43), 77 (95), and 51 (63)	C ₁₉ H ₂₂	91.13 (91.25)	8.87 (8.75)
(6e) ^h	2 900, 2 840, 2 010, 1 440, 1 340, 1 290, 1 095, 1 060, 820, and 740	2.45 (br s, 4 H), 2.14—1.10 (m, 18 H), and 0.91 (ABq, J 9.0, $J/\Delta\delta = 0.316$, 2 H)	254 (1.1), 253 (8.6), 252 (39), ^d 251 (2.7), 237 (24), 198 (24), 91 (72), and 41 (100)	C ₁₉ H ₂₄	90.40 (90.4)	9.60 (9.6)
(6f)	3 080, 2 970, 2 920, 2 850, 2 010, 1 770, 1 630, 1 450, 1 100, 1 080, 880, and 790	4.90—4.72 (m, 2 H), 2.56 (br s, 2 H), 2.2—1.6 (m, 12 H), 1.73 (t, J 1.5, 3 H), 1.60 (s, 1 H), 1.48 (s, 1 H), and 1.38 (s, 3 H)	242 (2.8), 241 (21), 240 (100), ^d 239 (8.0), 225 (82), 197 (15), 143 (38), 129 (40), 119 (61), and 115 (47)	C ₁₈ H ₂₄	89.92 (89.95)	10.08 (10.1)
(6g)	2 910, 2 840, 2 000, 1 440, 1 380, 1 090, 980, and 850	5.05—4.92 (m, 1 H), 2.52 (br s, 2 H), 2.16 (d, J 7.5, 1 H), 2.06—1.81 (m, 12 H), 1.75 (br s, 6 H), 1.28 (s, 3 H), and 1.15 (s, 3 H)	269 (3.9), 268 (16), ^d 254 (36), 253 (100), 133 (32), 105 (23), 91 (41), 79 (39), 77 (27), and 55 (44)	C ₂₀ H ₂₈	89.47 (89.25)	10.53 (10.75)
(6h) ^{e,h}	2 920, 2 840, 2 010, 1 635, 1 445, 1 095, 990, and 890	5.88—4.50 (m, 3 H), 2.54 (br s, 2 H), 2.25—1.75 (m, 14 H), 1.51 (s, 2 H), and 1.35 (s, 3 H) ^{c,f}	227 (2.5), 226 (12), ^d 211 (12), 183 (5.0), 169 (6.9), 129 (16), 105 (27), 91 (60), 79 (48), 53 (39), and 41 (100)	C ₁₇ H ₂₂	90.19 (90.05)	9.81 (9.95)
(6i) ^g	2 920, 2 840, 2 010, 1 445, 1 365, 1 095, 1 065, 1 030, 960, 795, and 715	2.52 (br s, 2 H), 2.30—1.70 (m, 16 H), 1.65—0.80 (m, 3 H), 1.38 (s, 6 H), and 1.05 (s, 3 H) ^c	295 (1.1), 294 (3.9), ^d 291 (1.8), 279 (2.8), 91 (33), 79 (41), 67 (40), 55 (47), 43 (81), and 41 (100)	C ₂₂ H ₃₀	89.71 (89.6)	10.29 (10.4)
(6j) ^g	2 900, 2 840, 2 010, 1 440, 1 090, 960, and 800	2.45 (br s, 2 H), 2.30—1.75 (m, 16 H), 1.72—1.35 (m, 6 H), 1.20 (s, 3 H), and 1.00 (s, 3 H) ^c	295 (4.1), 294 (14), ^d 293 (1.1), 291 (1.6), 279 (12), 251 (40), 131 (32), 129 (33), 117 (47), 91 (100), 69 (57), and 57 (53)	C ₂₂ H ₃₀	89.71 (89.65)	10.29 (10.35)
(6k) ^g	2 900, 2 840, 2 010, 1 440, 1 090, and 960	2.49 (br s, 2 H), 2.20—1.65 (m, 16 H), 1.65—0.80 (m, 6 H), and 0.85 (s, 6 H) ^c	296 (1.2), 295 (8.0), 294 (32), ^d 279 (13), 251 (16), 93 (35), 91 (71), 79 (76), and 41 (100)	C ₂₂ H ₃₀	89.71 (89.65)	10.29 (10.35)
(6l)	2 930, 2 840, 2 000, 1 445, 1 220, 1 140, 1 085, 1 065, 825, 775, and 755	3.98 (d, J 3.5, 1 H), 3.83—3.23 (m, 2 H), 2.57 (br s, 2 H), 2.27—1.20 (m, 17 H) ^c	243 (10), 242 (50), ^d 241 (20), 227 (3.9), 214 (29), 199 (17), 185 (46), 91 (37), 43 (35), and 41 (100)	C ₁₇ H ₂₂ O	84.23 (84.15)	9.17 (9.25)
(6m)	3 040, 2 900, 2 840, 2 020, 1 490, 1 440, 1 340, 1 310, 1 150, 1 130, 1 060, 960, 880, and 780	3.79 (t, J 4.5, 1 H), 3.56 (q, J 7.5, 2 H), 2.58 (br s, 2 H), 2.13—1.73 (m, 12 H), 1.58 (d, J 4.5, 2 H), and 1.17 (t, J 7.5, 3 H) ^c	231 (1.4), 236 (7.6), ^d 215 (3.1), 131 (39), 129 (44), 117 (58), 115 (51), 93 (71), 91 (100), 78 (35), and 41 (72)	C ₁₆ H ₂₂ O	83.41 (83.4)	9.64 (9.65)
(6n) ^h	3 020, 2 890, 2 910, 2 830, 2 000, 1 660, 1 440, 1 230, 1 130, 1 035, and 710	5.5—5.4 (m, 2 H), 3.25 (s, 3 H), 2.7—2.3 (m, 6 H), and 2.25—1.75 (m, 13 H)	270 (4.5), 269 (15), 268 (28), ^d 267 (22), 253 (35), 237 (21), 115 (26), 108 (60), 91 (65), 79 (58), and 39 (100)	C ₁₉ H ₂₄ O	85.01 (84.9)	9.03 (9.1)
(6o)	3 260, 2 920, 2 840, 2 010, 1 445, 1 370, 1 120, 1 090, and 1 020, 790	3.61 (dd, J 2.0 and 3.8, 2 H), 2.48 (br s, 2 H), 2.33—1.50 (m, 14 H), ⁱ 1.25 (s, 3 H), and 1.22 (s, 3 H) ^c	245 (3.6), 244 (19), ^d 230 (2.1), 229 (11), 214 (17), 213 (92), 105 (30), 93 (62), 91 (100), and 41 (46)	C ₁₇ H ₂₄ O	83.53 (83.35)	9.92 (10.1)

^a All compounds were purified on a preparative t.l.c. of silica gel—hexane unless otherwise stated and obtained as crystals (see Table 2). I.r. spectra were scanned in KBr discs. ^b All ¹H n.m.r. spectra were measured in CDCl₃ unless otherwise stated. Multiplicities and J values (Hz) are given in parentheses. ^c In CCl₄. ^d M^+ ion peaks. ^e ca. 17% of Regioisomer (6h') was involved. ^f Peaks due to (6h') also appeared at δ 1.67 (br s) and 4.70 (m). ^g Stereochemistry assignments should be considered as tentative. ^h Purified on an alumina plate eluting with hexane. ⁱ D₂O exchangeable 1 H is involved.

chemistry was tentatively assigned as *exo* on assumption of the less hindered addition of compound (4). Vinyl ether derivatives (51–n) gave generally better yields of the cycloadducts (61–n). No cycloadduct to the olefinic entity of compound (5n) was formed. These results are in good accord with the electrophilic nature of dialkylvinylidenecarbenes.²

The described method of adamantylidenevinylidenecyclopropanation requires alkaline conditions but the relative ease with which the derivatives can be obtained demonstrates practical utility for substrates stable to alkali.

Experimental

M.p.s were taken in a sealed tube on a Yanagimoto micro-melting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240B elemental analyser. ¹H n.m.r. spectra were taken at 25 °C with a JEOL JNM-C-60HL instrument at 60 MHz using Me₄Si as internal standard, i.r. spectra were recorded on a JASCO A-100 spectrometer, and mass spectra were obtained with an ESCO-EMD-05B instrument at 70 eV.

2-Ethynyladamantan-2-ol (2).—A modified procedure using commercial sodium acetylide was employed rather than the literature procedure⁷ of *in situ* generation in liquid ammonia. An anhydrous THF solution of adamantanone (1) (4.51 g, 30.0 mmol, in 50 ml) was slowly added to a stirred and cooled (15 °C) suspension of sodium acetylide in xylene (11–15%, 40 ml, 110–150 mmol), during 1 h under nitrogen. The mixture was stirred for 18 h at room temperature and 1 h at 70 °C [the disappearance of (1) was confirmed by g.l.c. analysis] then cautiously diluted with water (50 ml) under ice-cooling, and then with ether (30 ml). The mixture was acidified with 50% H₂SO₄, the organic layer separated, and the aqueous layer extracted with ether (3 × 20 ml). The combined organic layer and extracts were washed with saturated aqueous sodium chloride, dried (Na₂SO₄), and the solvent evaporated under reduced pressure to give (2) as a white solid (5.30 g, 100%), m.p. 100–102 °C (Lit.,^{7a} 102–104 °C), which was practically pure by i.r. and ¹H n.m.r. spectra.

2-Chloro-2-ethynyladamantane (3).—This was prepared by the literature procedure^{7a} and was obtained as colourless crystals (61%), m.p. 65–66 °C (Lit.,^{7a} 65–66 °C).

General Procedure for Adamantylidenevinylidenecyclopropanation using Compound (3).—The chloride (3) (50 mg, 0.26 mmol) in benzene (5 ml) was added dropwise to a vigorously stirred mixture of the appropriate olefin (2.57 mmol), Bu^tOK (58 mg,

of 95% reagent of Merck Co., 0.51 mmol), and 18-crown-6 (14 mg, 0.051 mmol) in benzene (2 ml) over 1.5 h under argon at room temperature (20–28 °C). Stirring was continued for the appropriate time (t.l.c. monitored, Table 2) and the mixture diluted with water and extracted with hexane or ether (3 × 20 ml). The combined extracts were washed with saturated aqueous sodium chloride, dried (Na₂SO₄), and the solvent evaporated under reduced pressure to give a crude product which was purified by preparative t.l.c. (silica gel or alumina eluting with hexane or hexane–AcOEt system in general, Table 3) to afford the adamantylidenevinylidenecyclopropanes (6a–6o).

The adamantylidenevinylidenecyclopropanation of styrene (5a) was also carried out under the conditions summarized in Table 1. In entries 1 and 2, 51% aqueous KOH (10 ml) was used instead of Bu^tOK. The ultrasonic irradiation (entry 6) was conducted with a Branson B-220 ultrasonic cleaner.

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