Mild Generation of Adamantylidenevinylidene (an Alkenylidenecarbene) from 2-Bromo-2-(trimethylsilylethynyl)adamantane and (2-Bromo-2-trimethylsilylvinylidene)adamantane

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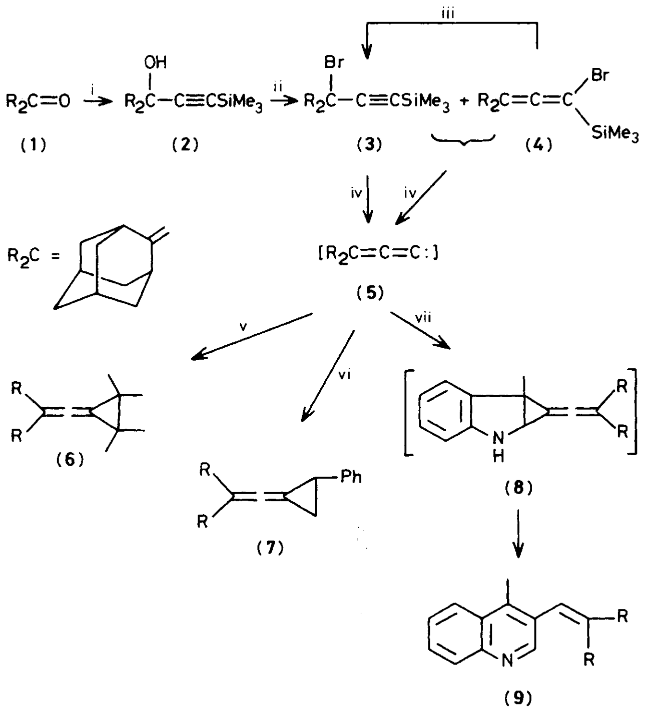
Adamantylidenevinylidene, a new alkenylidenecarbene, was successfully generated by fluoride-initiated elimination of trimethylsilyl and bromo groups from 2-bromo-2-(trimethylsilylethynyl)adamantane and (2-bromo-2-trimethylsilylvinylidene)adamantane.

The known methods for generation of alkenylidenecarbenes involve γ- or α-dehydrohalogenation of prop-2-ynyl halide or allenyl halide by strong base,[1,2] or decomposition of diazoallene generated from bis(nitrosourethane).[3] However, the former route requires strong bases such as t-butoxide or hydroxide even under phase-transfer catalysed conditions,[2] and the latter route suffers the disadvantages of complicated preparation of the precursor and also limited application. Here, we describe a mild method of generation of adamantylidenevinylidene, a new alkenylidenecarbene, by a fluoride-initiated elimination of trimethylsilyl and bromo groups.[4]

Addition of lithium trimethylsilylacetylide to adamantan-



Scheme 1. *Reagents and conditions:* i, LiC≡CSiMe$_3$, tetrahydrofuran, −10 °C → room temperature, 17 h; ii, PBr$_3$ (3.78 equiv.)–pyridine (catalytic amount), diethyl ether, 5 °C → room temperature, 2 days; iii, 135 °C, DMF–KBr (catalytic amount), 1 h; iv, Bu$^n_4$NF (1.50 equiv.), glyme, −10 °C (1.0 h) → room temperature, 2 days; v, 2,3-dimethylbut-2-ene (1.91 equiv.); vi, styrene (22.0 equiv.); vii, skatole (1.20 equiv.).

one (**1**) gave 2-hydroxy-2-(trimethylsilylethynyl)adamantane (**2**) as colourless crystals (98%), m.p. 54.5—55.5 °C.† Bromination of (**2**) with PBr$_3$ (3.78 equiv.) in the presence of a catalytic amount of pyridine in diethyl ether at 5—20 °C for 2 days afforded a 3:7 mixture of bromides (**3**) [i.r. (film) $\nu_{max.}$ 2160 cm^{-1} (C≡C)] and (**4**) [i.r. (film) $\nu_{max.}$ 1940 cm^{-1} (C=C=C)] as an oil in 96% yield. These bromides could not be separated by chromatography (silica gel and/or alumina) and/or distillation under reduced pressure. However, the mixture was converted into practically pure (**3**) by heating for 1 h in dimethylformamide (DMF) at 135 °C in the presence of a catalytic amount of KBr, and the usual work up gave (**3**) as an oil (93%).

Treatment of (**3**) with Bu$^n_4$NF (1.50 equiv.) in glyme (2 ml) and 2,3-dimethylbut-2-ene (1.91 equiv.) at −10 °C for 1 h and at room temperature for 2 days afforded the carbene adduct (**6**) in 75% isolated yield as crystals, m.p. 120—121.5 °C (Scheme 1). The same adduct (**6**) was also obtained in 71% yield by using the 3:7 mixture of (**3**) and (**4**) under similar conditions. These results indicate the generation of adamantylidenevinylidene (**5**) from both (**3**) and (**4**). The reaction in the presence of styrene (22 equiv.) afforded the corresponding adduct (**7**) as an oil in 76% yield. Furthermore, the reaction in the presence of skatole (1.2 equiv.) yielded a quinoline derivative (**9**) (9.0%), picrate m.p. 218—222 °C, after preparative t.l.c. (alumina), presumably *via* the corresponding unstable adduct (**8**).

This fluoride-initiated elimination route provides a method of formation of adamantylidenevinylidene, a new alkenylidenecarbene, under mild conditions. Application of this method to the generation of dimethyl- and pentamethylenealkylidenecarbenes, as well as the synthetic utility of the alkenylidenecarbenes generated by this method, will be reported in due course.

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† All new compounds described here had spectral and microanalytical properties in agreement with the assigned structures.

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