

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

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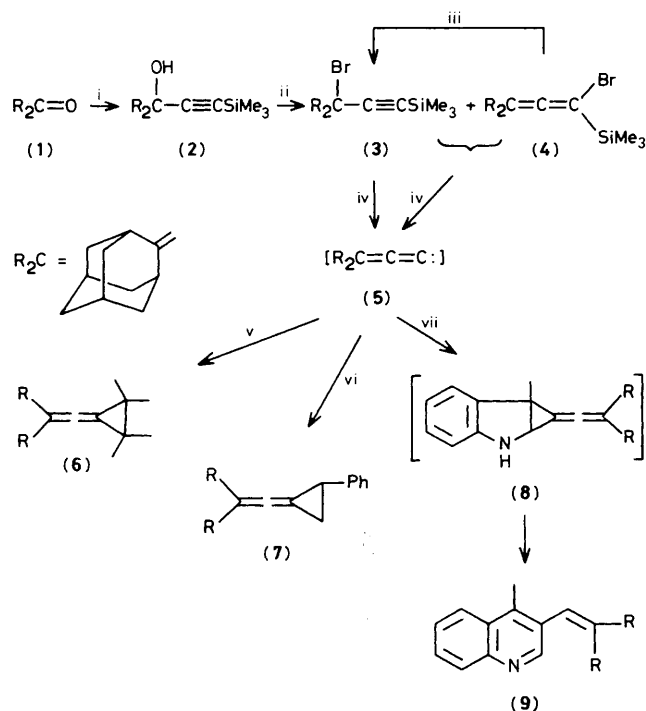
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Adamantylidenevinylidene, a new alkenyldenecarbene, was successfully generated by fluoride-initiated elimination of trimethylsilyl and bromo groups from 2-bromo-2-(trimethylsilylethynyl)adamantane and (2-bromo-2-trimethylsilylvinylidene)adamantane.

The known methods for generation of alkenyldenecarbenes 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 alkenyldenecarbene, by a fluoride-initiated elimination of trimethylsilyl and bromo groups.⁴

Addition of lithium trimethylsilylacetylide to adamantan-



Scheme 1. Reagents and conditions: i, $\text{LiC}\equiv\text{CSiMe}_3$, tetrahydrofuran, $-10^\circ\text{C} \rightarrow$ room temperature, 17 h; ii, PBr_3 (3.78 equiv.)–pyridine (catalytic amount), diethyl ether, $5^\circ\text{C} \rightarrow$ room temperature, 2 days; iii, 135°C , DMF–KBr (catalytic amount), 1 h; iv, Bu^n_4NF (1.50 equiv.), glyme, -10°C (1.0 h) \rightarrow 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. $54.5\text{--}55.5^\circ\text{C}$.† Bromination of (2) with PBr_3 (3.78 equiv.) in the presence of a catalytic amount of pyridine in diethyl ether at $5\text{--}20^\circ\text{C}$ for 2

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

days afforded a 3:7 mixture of bromides (3) [i.r. (film) ν_{max} , 2160 cm^{-1} ($\text{C}\equiv\text{C}$)] and (4) [i.r. (film) ν_{max} , 1940 cm^{-1} ($\text{C}=\text{C}$)] 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_4NF (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. $120\text{--}121.5^\circ\text{C}$ (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. $218\text{--}222^\circ\text{C}$, 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 alkenylidene carbene, under mild conditions. Application of this method to the generation of dimethyl- and pentamethylenealkylidene carbenes, as well as the synthetic utility of the alkenylidene carbenes generated by this method, will be reported in due course.

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