A Novel Intramolecular [2π + 2π] Photocycloaddition of Di- and Tetra-allylsilanes

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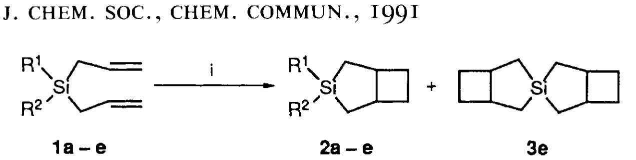
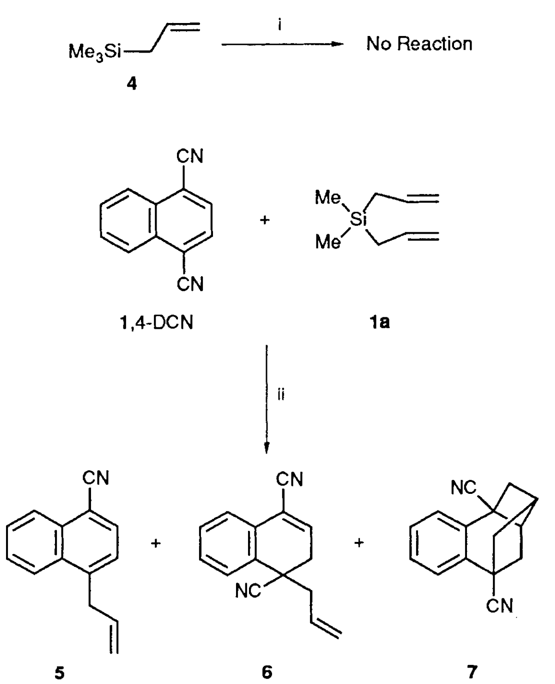
Irradiation of di- and tetra-allylsilanes in the presence of 1,4-dicyanonaphthalene (1,4-DCN) in benzene afforded the intramolecular [2π + 2π] photocycloadducts in good yields *via* (1,4-DCN–C_6H_6–Si-compound) triplexes.

Allylic silanes are versatile compounds in organic synthesis.[1] Photochemically, they can be used as allylating agents of electron-deficient molecules such as iminium salts,[2] aromatic nitriles,[3,4] quinones,[5] electron-deficient alkenes[6] and aromatic imides,[7] *via* photoinduced electron transfer. However, little is known about the photochemical reactivity of the alkenic moiety in allylic silanes.[8] We now report the intramolecular [2π + 2π] photocycloaddition of di- and tetra-allylsilanes in the presence of 1,4-dicyanonaphthalene (1,4-DCN) that probably proceeds *via* triplexes.



a, $R^1 = R^2 = Me$; **b**, $R^1, R^2 = -(CH_2)_4-$; **c**, $R^1 = R^2 = Ph$; **d**, $R^1 = Me$, $R^2 = Ph$; **e**, $R^1 = R^2 = CH_2{=}CHCH_2-$

Scheme 1 *Reagents and conditions*: i, *hv*, 1,4-DCN, C_6H_6

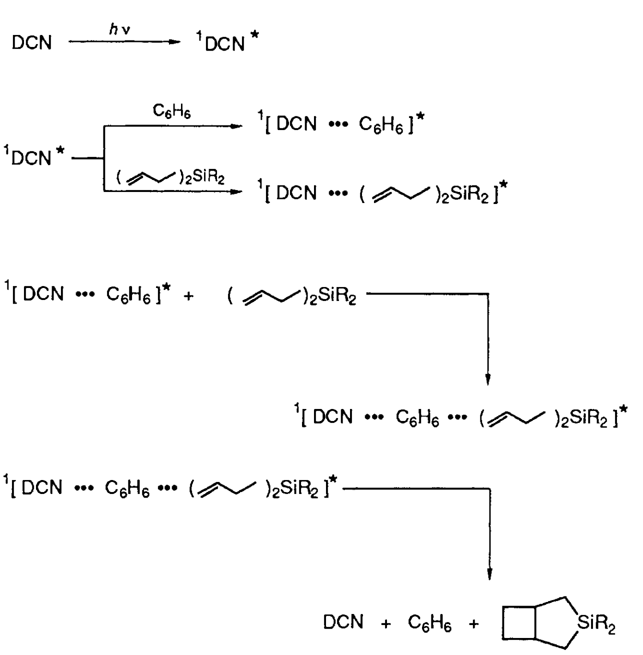


Scheme 2 *Reagents and conditions*: i, *hv*, 1,4-DCN, C_6H_6; ii, *hv*, MeCN

Irradiation of a benzene solution of diallyldimethylsilane **1a** in the presence of a catalytic amount of 1,4-DCN through Pyrex by a high-pressure mercury lamp (λ > 280 nm) under nitrogen atmosphere for 48 h afforded 3,3-dimethyl-3-silabicyclo[3.2.0]heptane **2a** in 75% yield (Scheme 1). Irradiation of the silanes **1b–e** in a similar manner gave the corresponding [2π + 2π] cycloadducts **2b–e** and **3e** in 54, 69, 47 and 65% yields, respectively. It was found that **2e** is converted to **3e** by irradiation in the presence of 1,4-DCN. These cycloadducts were isolated by column chromatography on silica gel. The structures were determined by their spectral properties (^1H NMR, ^{13}C NMR, IR and mass)† and their elemental analyses.

The photoreaction of allyltrimethylsilane **4** in the presence of 1,4-DCN in benzene afforded no cycloadducts even after prolonged irradiation. However, when the photoreaction was carried out in acetonitrile, the allylation of 1,4-DCN efficiently occurred to give **5**, **6**, **7** as previously reported (Scheme 2).[4]

To gain mechanistic information, the effects of solvents, sensitizers and additives on the photoreactions were examined. The intramolecular photocycloaddition of **1a** to give **2a** did occur efficiently in aromatic solvents such as benzene, toluene and xylene, but did not occur in cyclohexane, diethyl ether, dichloromethane and ethyl acetate. However, this photocycloaddition began to proceed, though with less efficiency, upon adding 10 vol% of benzene, toluene or xylene into cyclohexane or dichloromethane solutions of **1a**. In acetonitrile, **5–7** were produced, accompanying the disappearance of 1,4-DCN.



DCN = 1,4-DCN

Scheme 3

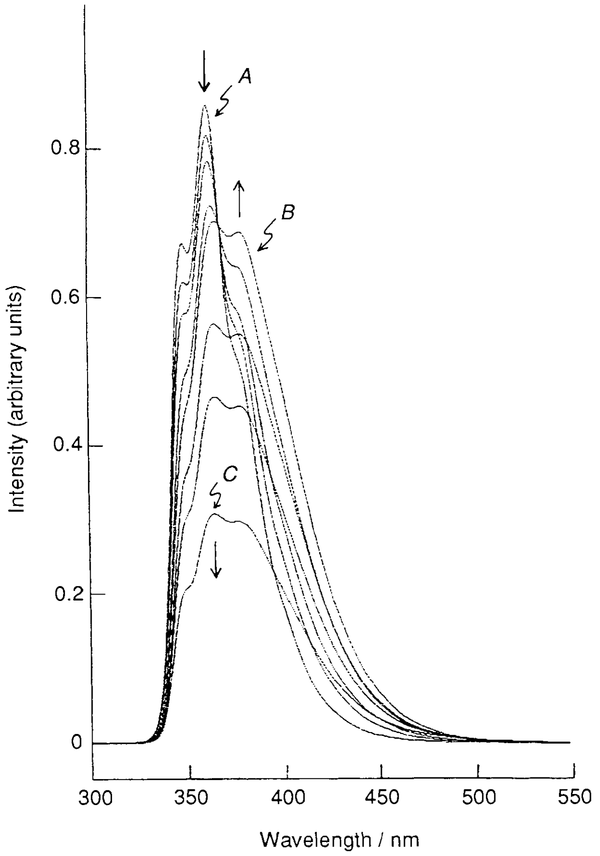


Fig. 1 Fluorescence spectra of 1,4-DCN in cyclohexane: *A*, 1,4-DCN ([1,4-DCN] = 1.0 × 10^{-4} mol dm^{-3}); *B*, exciplex emission between 1,4-DCN and toluene ([1,4-DCN] = 1.0 × 10^{-4} mol dm^{-3}, [toluene] = 0.2 mol dm^{-3}); *C*, exciplex emission between 1,4-DCN and toluene quenched by **1e** ([1,4-DCN] = 1.0 × 10^{-4} mol dm^{-3}, [toluene] = 0.2 mol dm^{-3}, [**1e**] = 3.3 × 10^{-2} mol dm^{-3})

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† *Spectroscopic data* for **3e**: ^1H NMR (270 MH, $CDCl_3$) δ 0.64 (dd, *J* 3.0 and 15.5 Hz, CH_2), 0.83 (dd, *J* 3.0 and 15.5 Hz, CH_2), 0.92 (dd, *J* 9.4 and 16.9 Hz, CH_2), 1.09 (dd, *J* 9.5 and 15.5 Hz, CH_2), 1.40–1.59 (m, CH_2), 2.11–2.22 (m, CH_2) and 2.73–2.95 (m, CH); ^{13}C NMR (270 MHz, $CDCl_3$) δ 18.8 (CH_2), 19.8 (CH_2), 27.2 (CH_2), 29.8 (CH_2), 38.2 (CH) and 39.0 (CH).

Fluorescence of 1,4-DCN, 9,10-dicyanoanthracene (DCA), 2,3-dicyanonaphthalene (2,3-DCN) and 1,4-dicyanobenzene (DCB) was efficiently quenched in benzene by **1a–e**. However, the only one of these aromatic nitriles to sensitize the photocycloaddition was 1,4-DCN. All the results strongly suggest that 1,4-DCN and benzene or its methylated compounds are indispensable for this intramolecular photocycloaddition. The formation of exciplexes between 1,4-DCN and benzene derivatives,[9] and the formation of triplexes among 1,4-DCN, benzene derivatives, and 1,2-diarylcyclobutane or hexamethyldewarbenene[10] have been reported. On the basis of these experimental results, we propose the mechanism shown in Scheme 3 for the photocycloaddition. Termolecular interaction among 1,4-DCN, toluene and **1e** in the excited state was suggested from the fluorescence quenching experiments (Fig. 1). Fluorescence of 1,4-DCN in cyclohexane was quenched by toluene and **1a–e**. In the 1,4-DCN–toluene system, an exciplex emission was observed, showing an isoemissive point at 368 nm. This exciplex emission was efficiently quenched by **1e**, but a triplex emission was not observed at longer wavelength.

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