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A Novel Photocycloaddition of Allylic Silanes to 2,3-Dicyano-5,6-dimethylpyrazine: Formation of 2,8-Diazatricyclo[3.2.1.$0^{4,8}$]oct-2-ene Derivatives

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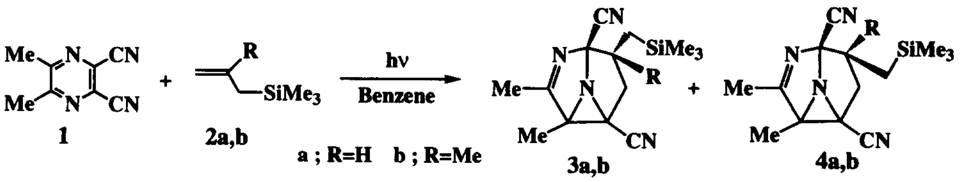
Abstract : Irradiation of a benzene solution containing 2,3-dicyano-5,6-dimethylpyrazine with allylic silanes afforded 2,8-diazatricyclo[3.2.1.$0^{4,8}$]oct-2-ene derivatives in moderate yields. This photoreaction involves the ($2\pi + 2\pi$) photocycloaddition followed by rearrangement.

Photocycloaddition is a simple and useful method for the synthesis of polycyclic compounds including N-containing heterocycles.[1] However, little is known about the photocycloaddition of alkenes to pyrazine ring, though the photoreduction and photosubstitution of dicyanopyrazines initiated by photoinduced electron transfer have been independently reported by Tada et al.[2] and by us.[3] We now report a novel photocycloaddition of allylic silanes to 2,3-dicyano-5,6-dimethylpyrazine (**1**) which involves a skeleton rearrangement and gives strained N-containing tricyclic compounds.

Irradiation of a benzene solution containing **1** (10 mmol/dm^3) and allyltrimethylsilane (**2a**) (100 mmol/dm^3) through a Pyrex filter with a 300W high-pressure mercury lamp (> 280 nm) under argon atmosphere gave 1,5-dicyano-3,4-dimethyl-7-trimethylsilylmethyl-2,8-diazatricyclo[3.2.1.$0^{4,8}$]oct-2-ene (**3a**) in a 40% isolated yield along with its stereoisomer (**4a**) in a 10% yield.[4] Similar irradiation of **1** with 2-methyl-2-propenylsilane (**2b**) afforded the corresponding tricyclic compounds **3b** and **4b** in moderate yields. These products were isolated by column chromatography on silica gel. Their structures were determined by their spectral properties. The structure of **3a** was finally confirmed by the X-ray crystallographic analysis.[5]

The formation of **3a** was effectively sensitized by acetophenone (E_T = 310 kJ/mol) and benzophenone (E_T = 287 kJ/mol), but not sensitized by 1- and 2-acetonaphthone (E_T = 236 and 249 kJ/mol). The relative



Scheme 1.

quantum yield for the formation of **3a** decreased to one fifth by the addition of 0.08 mol/dm^3 of 2-methyl-1,3-butadiene. Irradiation of **1** in the absence of alkenes did not afford any transposition product, and **1** was completely recovered. The photoreactions of **1** with electron-deficient alkenes such as acrylonitrile and methyl acrylate or aromatic alkenes such as styrene and 2-phenyl-1-propene in benzene did not give the corresponding photocycloadducts.

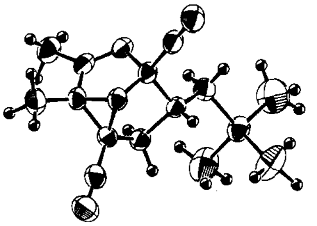
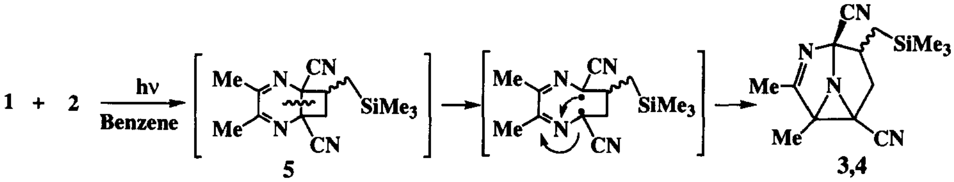


Fig. 1 . ORTEP drawing of **3a**

From these results, the formation of the tricyclic compounds can be reasonably explained by the (2π + 2π) photocycloaddition via the excited triplet state of **1** followed by the thermal or photochemical rearrangement as shown in Scheme 2. Although the construction of tricyclo[3.2.1.$0^{4,8}$]oct-2-ene skeleton can be achieved by the well-known 1,3-photoaddition of alkenes to benzene ring[6] or the di-π-methane rearrangement of bicyclo[2.2.2]oct-2,5-dienes,[7] the formation of **3** and **4** can not be explained by these mechanisms. In this stage, we did not isolate the (2π + 2π) photocycloadducts (**5**) even in the low conversion (< 20%). Probably, **5** quickly rearranges to the tricyclic compounds **3** and **4**.



Scheme 2.

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4. **3a**; mp 220-221 ℃; MS *m/z* 272 (M^+), 257, 184, 73; IR (KBr) 2242, 1634 cm^{-1}; ^1H NMR (270 MHz, CD_3Cl) δ 0.03 (s, 9H), 0.56 (dd, J=12.8, 14.6 Hz, 1H), 1.01 (dd, J=3.0, 14.6 Hz, 1H), 1.40 (dd, J=11.6, 13.4 Hz, 1H), 1.62 (s, 3H), 2.21 (s, 3H), 2.45 (dd, J=7.9, 13.4 Hz), 3.15-3.28 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -1.24, 14.77, 15.76, 16.51, 32.34, 45.82, 57.44, 97.35, 115.86, 116.35, 172.26.
5. Crystal data for **3a**; $C_{14}H_{20}N_4Si$ monoclinic; space group $P2_1$/a (No. 14); a =10.933(1) b =13.199(1) c =12.149(1) Å, β=113.842(9)°, U=1603.5(4) Å^3, Z=4, D_c=1.128 g cm^{-3}, μ(Mo-K$_\alpha$)=1.35 cm^{-1}, $R(R_w)$=0.045 (0.051); S=2.02.
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