New 6-oxa-2-silabicyclo[2.2.0]hexanes by photochemical conversion of acyl(allyl)(dimethyl)silanes†

Catherine Hammaecher and Charles Portella*

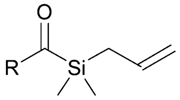
Received (in Cambridge, UK) 22nd July 2008, Accepted 26th August 2008
First published as an Advance Article on the web 30th September 2008
DOI: 10.1039/b812550c

Under UV irradiation in acetonitrile, acyl(allyl)silanes undergo an intramolecular (2 + 2) cycloaddition (Paternò-Büchi type reaction) to give unprecedented 1-alkyl-6-oxa-2-silabicyclo[2.2.0] hexanes.

As is the case for their fundamental state chemistry, the photochemistry of acylsilanes offers, in addition to processes similar to those of ketones, specific reactions depending on the substrate structure and reaction conditions. Besides some examples involving γ-hydrogen abstraction (Norrish II)[1] the main chemical processes resulting from acylsilane irradiation are connected, at least formally, with a CO–Si bond fragmentation, the reaction products depending strongly on the reaction medium. In non polar solvents, results are solvent dependant: acylsilanes react similarly to ketones in tetrachloromethane,[2] or *via* more complex intermolecular or dismutation routes in hydrocarbons.[3] In protic solvents or in the presence of aldehydes, products result from the trapping of a siloxycarbene formed by 1,2-C to *O*-silyl migration.[4] Trapping by electron deficient alkenes was disclosed in 1971 by A. G. Brook and co-workers,[5] but it was shown later that the cyclopropane derivative resulted from a reaction between alkene and the excited state of the acylsilane.[6] Such a carbene may be trapped by water or alcohol giving an aldehyde or an *O*-silyl acetal, respectively. This reaction was exploited to prepare glycoside-derived *O*-silylacetals having anti-tumor activity[7] and homologated nucleoside derivatives.[8]

To the best of our knowledge, all photochemical investigations conducted so far have been on simple acylsilane or acylsilanes functionalised on the acyl moiety. Thus it appeared interesting to study the photochemical reactivity of acyl(allyl)silanes, which could be expected to follow several routes. We were particularly interested in a possible intramolecular trapping of an intermediate carbene or excited species.

Surprisingly, acyl(allyl)silanes seem to have been reported only once by Tsai's group who studied intramolecular radical addition on the allyl unsaturation.[9] We have prepared a series of acyl(allyl)silanes depicted in Fig. 1. The acyl(allyl)silanes **1a**, **1b**, **1d** and **1e** were prepared *via* a modified Brook–Corey strategy.[10] Undecanoyl(allyl) silane **1c** was obtained *via* a modified Katritsky strategy.[11] UV absorption characteristics of the carbonyl chromophore are similar to classical acylsilanes, as exhibited by **1a** and **1b** as representative of the aroyl and acyl compounds, respectively.[12]

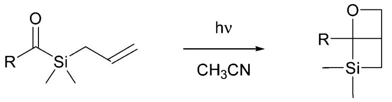


	R
1a	Ph
1b	Bn
1c	*n*-$C_{10}H_{21}$
1d	$Ph(CH_2)_2$
1e	*cycl*Hex

Fig. 1 Acyl(allyl)dimethylsilanes.

Irradiation of benzoyl derivative **1a** at 420 nm in acetonitrile induced a decoloration of the starting solution but gave an intractable reaction mixture. Aliphatic compounds were irradiated at 350 nm. The phenylacetylsilane **1b** underwent a Norrish type 1 fragmentation on the acyl side, or a CO–Si fragmentation–decarbonylation sequence, as the presence of diphenylethane in the crude product shows (NMR analysis).[13] Much more interestingly, irradiation of allyl(dimethyl)undecanoylsilane **1c** in the same conditions induced a rapid, clean and quantitative conversion into a new type of heterobicyclo[2.2.0]hexane, 6-oxa-2-silabicyclo[2.2.0]hexane **2c** (Scheme 1). Compound **2c** is the result of an intramolecular Paternò-Büchi type cycloaddition.[14,15] The reaction was extended to the acyl(allyl)silanes **1d** and **1e** which led to the corresponding bicyclic analogues **2d** and **2e**, respectively. In contrast to **2c**, **2d** and **2e** were obtained in lower yields, the reaction giving an unidentified side-product. According to NMR spectra, this side-product was the same from both reactions, and did not contain the alkyl moiety.

Compounds **2** are colorless liquids. They were isolated and purified by flash chromatography and their purity was checked by GLC. Their structure was determined according to NMR spectra, GCMS under chemical ionisation conditions, and chemical correlations. The NMR data of compound **2d**, the spectra of which is the best resolved, is depicted in Fig. 2. The structure of oxetanes **2** were corroborated by chemical



1c → **2c** 99%
1d → **2d** 53%
1e → **2e** 52%

Scheme 1 Photochemical reaction of acyl(allyl)silanes in acetonitrile.

Université de Reims Champagne-Ardenne, Institut de Chimie Moléculaire de Reims, CNRS UMR 6229, UFR Sciences Exactes et Naturelles, BP 1039, 51687 REIMS Cedex 2, France.
E-mail: charles.portella@univ-reims.fr; Fax: +33 326913234;
Tel: +33 326913166

† Electronic supplementary information (ESI) available: Experimental part including ^{1}H and ^{13}C NMR spectra of compounds **1a–1e**, **2a–2e**. See DOI: 10.1039/b812550c

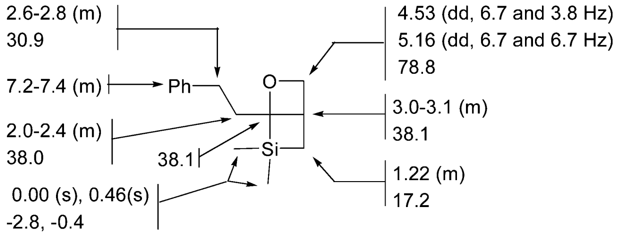
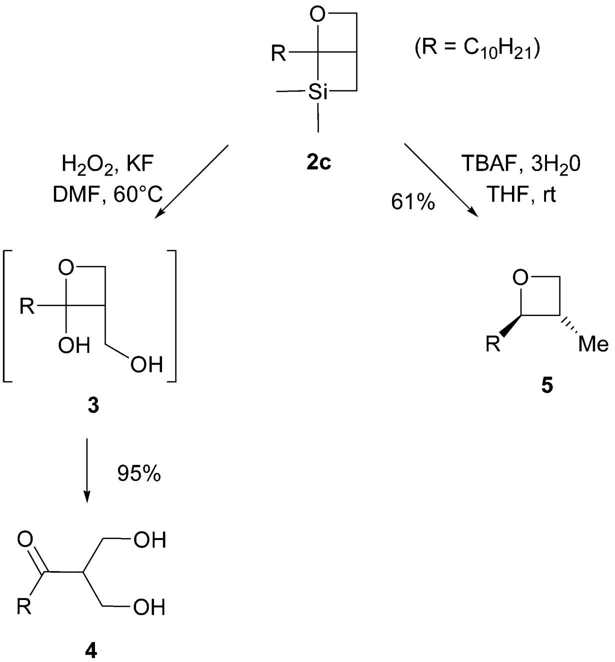
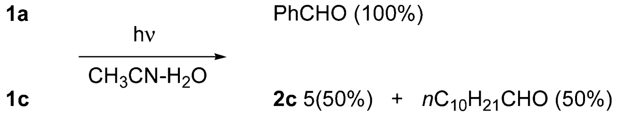


Fig. 2 ^{1}H- and ^{13}C-NMR data (δ ppm) for compound **2d**.



Scheme 2 Chemical transformations of compound **2c**.

transformations involving the cleavage of Si–C bonds. Tamao type oxidation[16] of **2c** gave the expected ketodiol **4**, *via* the intermediate hemiketal **3** derived from Si–C bond oxidative cleavage (Scheme 2). Fluoride induced protodesilylation of **2c** yielded the expected 2,3-dialkyloxetane **5**. A *trans* configuration was ascribed to **5** by comparison of ^{1}H- and ^{13}C-NMR spectra with those of very similar compounds reported in the literature.[17]

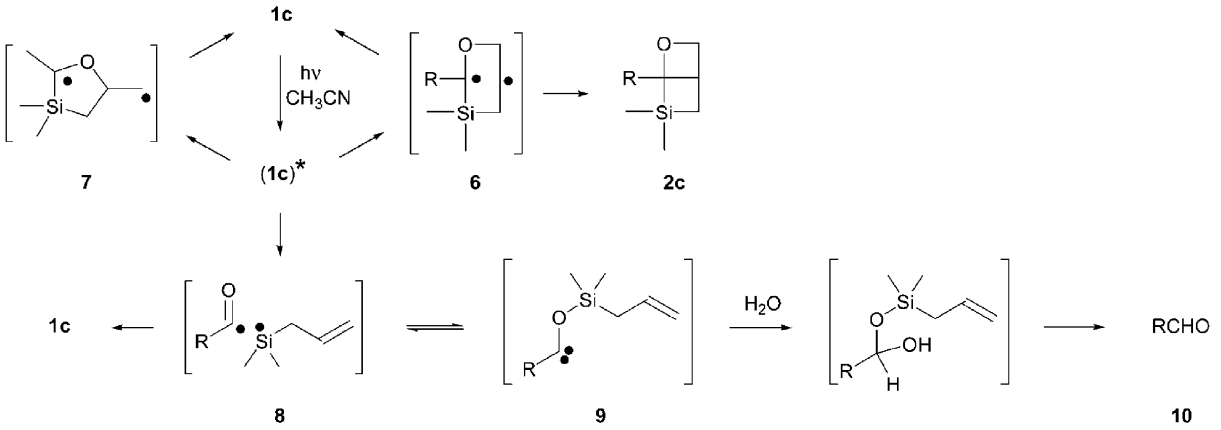


Scheme 3 Photochemical reaction of acyl(allyl)silanes in aqueous acetonitrile.

The photochemical behaviour of acyl(allyl)silanes **1** in acetonitrile resembles more the one of γ,δ-unsaturated ketones, which were reported to undergo an intramolecular Paternò-Büchi type cycloaddition,[18] than those of acylsilanes, with a marked difference as far as regioselectivity is concerned. The reaction of our acylsilanes proved to be completely regioselective toward the oxasilabicyclo[2.2.0]hexane regioisomer, whereas irradiation of isostructural γ,δ-unsaturated ketones also gave the bicyclo[3.1.1]hexane isomer; regioselective cycloaddition towards either isomer was observed only for rigid cyclic γ,δ-unsaturated ketones.[19]

The solvent proved to have a crucial role in the cycloaddition route. Indeed, under irradiation in a 1 : 1 mixture acetonitrile–water, benzoyl(allyl)silane **1a** was quantitatively converted into benzaldehyde, the expected result of the well known pathway: CO–Si fragmentation—rearrangement into a siloxycarbene—trapping of the latter to give the silyl hemiacetal. Under the same conditions, the undecanoyl analogue **1c** gave a 1 : 1 mixture of the corresponding aldehyde and the cycloaddition product **2c** (Scheme 3). This result is in accordance with the particularly high effectiveness of the intramolecular cycloaddition observed for **1c** in pure acetonitrile. This enhanced propensity of **1c** to cyclise compared to other aliphatic analogues remains difficult to explain.

A tentative interpretation of the observed photoreactivity of acyl(allyl)silanes in acetonitrile is proposed in Scheme 4. Independently of the primary photoprocesses which have not been considered here,[20] one can assume that longer C–Si bonds (compared to C–C bond) favour a selective cyclisation between the oxygen of the excited carbonyl group and the terminal allylic carbon, leading to the intermediate biradical **6** which further cyclises into **2**.[21] Such a process leads to a more stable secondary radical. The regioisomer radical **7**, if its formation occurred, would undergo β-fragmentation toward the starting material. The usual CO–Si framentation leading to the radical pair **8** is not competitive in anhydrous medium, but in the



Scheme 4 Proposed mechanism.

presence of water, the siloxycarbene **9** is trapped to give the corresponding aldehyde **10**. Another remarkable feature of this reactivity is the competitive cycloaddition *versus* formation of siloxycarbene, even in aqueous medium as shown for **1c**.

In summary, following the various studies on the photochemistry of acylsilanes reported so far, we report for the first time the synthesis of acyl(allyl)silanes. The latter undergoes, in anhydrous acetonitrile, selective intramolecular photocycloaddition yielding unprecedented 1-alkyl-6-oxa-2-silabicyclo[2.2.0]-cyclohexanes.

We thank the CNRS and the Ministry of Research for supporting this research, and the Région Champagne-Ardenne for a PhD fellowship (C.H.). We also express our thanks to Dr Norbert Hoffmann for his interest in and fruitful discussions on the research.

Notes and references

1 M. E. Scheller and B. Frei, *Helv. Chim. Acta*, 1984, **67**, 1734; M. E. Scheller, G. Iwasaki and B. Frei, *Helv. Chim. Acta*, 1986, **69**, 1378; M. E. Scheller and B. Frei, *Helv. Chim. Acta*, 1990, **73**, 922.
2 A. G. Brook, P. J. Dillon and R. Pierce, *Can. J. Chem.*, 1971, **49**, 133.
3 A. G. Brook and J. M. Duff, *Can. J. Chem.*, 1973, **51**, 352.
4 J. M. Duff and A. G. Brook, *Can. J. Chem.*, 1973, **51**, 2869; R. A. Bourque, P. D. Davis and J. C. Dalton, *J. Am. Chem. Soc.*, 1981, **103**, 697.
5 A. G. Brook, H. W. Kucera and R. Pearce, *Can. J. Chem.*, 1971, **49**, 1618.
6 J. C. Dalton and R. A. Bourque, *J. Am. Chem. Soc.*, 1981, **103**, 699.
7 S. A. Svarovsky, M. B. Taraban and J. J. Barchi, Jr, *Org. Biomol. Chem.*, 2004, **2**, 3155.
8 A. Wegert, J.-B. Behr, N. Hoffmann, R. Miethchen, C. Portella and R. Plantier-Royon, *Synthesis*, 2006, 2243.
9 K.-H. Tang, F.-Y. Liao and Y.-M. Tsai, *Tetrahedron*, 2005, **61**, 2037.
10 G. Brook, J. M. Duff, P. F. Jones and N. R. Davis, *J. Am. Chem. Soc.*, 1967, **89**, 431; E. J. Corey, D. Seebach and R. Freedman, *J. Am. Chem. Soc.*, 1967, **89**, 434.
11 A. R. Katritzky, H. Lang, Z. Wang and Z. Lie, *J. Org. Chem.*, 1996, **61**, 7551.
12 Absorption spectra were measured in CH_3CN [λ_{max}(nm); ε_{max}(L.mol^{-1} cm^{-1}]. **1a**: 416, 45; **1c**: 365, 49.
13 For photolysis of phenylacetyl(triphenyl)silane, see A. G. Brook *et al*: ref. 3.
14 E. Paternò and G. Chieffi, *Gazz. Chim. Ital.*, 1909, **39**, 341; G. Büchi, C. G. Inman and E. S. Lipinsky, *J. Am. Chem. Soc.*, 1954, **76**, 4327.
15 For a recent review, see: A. G. Griesbeck, in *Synthetic Organic Photochemistry*, ed. A. G. Griesbeck and J. Mattay, Marcel Dekker, New York, 2005, p. 89.
16 K. Tamao, N. Ishida, D. Tanaka and M. Kumada, *Organometallics*, 1983, **2**, 1694.
17 M. Christlieb, J. E. Davies, J. Eames, R. Hooley and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2983–2996.
18 N. C. Yang, M. Nussim and D. R. Coulson, *Tetrahedron Lett.*, 1965, **20**, 1525, and references therein.
19 V. H. Rawal, A. Fabré and S. lwasa, *Tetrahedron Lett.*, 1995, **36**, 6851; T. J. Reddy and V. H. Rawal, *Org. Lett.*, 2000, **2**, 2711; M. C. de la Torre, I. García and M. A. Sierra, *J. Org. Chem.*, 2003, **68**, 6611.
20 For photochemical primary processes of Paternò-Büchi reaction, see the review mentioned in ref. 15.
21 It has been shown that cyclization of 2-(allyldimethylsilyl)ethyl radicals proceed exclusively *via* 6-endo-trig mode: K. Saigo, K. Tateishi, H. Adachi and Y. Saotome, *J. Org. Chem.*, 1988, **53**, 1572.