Tetrahedron Letters,Vol.24,No.8,pp 795-798,1983 0040-4039/83/080795-04$03.00/0
Printed in Great Britain

INTRAMOLECULAR ACYLATION OF VINYLIC SILANES. A NOVEL, GENERAL APPROACH FOR THE SYNTHESIS OF FOUR- TO SIX-MEMBERED CARBOCYCLIC SYSTEMS AND ITS REGIOCHEMICAL FEATURES

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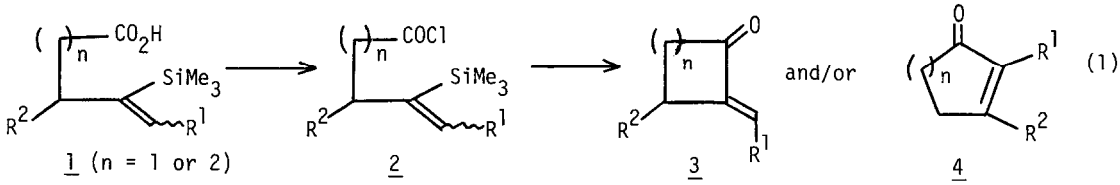
SUMMARY: Intramolecular acylations of m-trimethylsilyl-m-alkenoyl chlorides (m = 4 and 5) are described which afford the expected α-alkylidenecycloalkanone and/or the unexpected cycloalkenone, depending upon the substrate structure.

In view of the unique, well-defined reactivity of vinylic silanes toward a wide range of electrophiles,[1] the *intramolecular versions* of reactions of vinylic silanes with carbon-electrophiles in particular might be valuable extensions of the vinylsilane chemistry for the construction of various carbocyclic systems.[2] From the standpoint of the synthetic utility, the two types of intramolecular acylations depicted below are of special interest since the cycloacylations of A and B are highly anticipated, by direct analogy with the intermolecular versions,[1] to give the cycloalkenone and the α-alkylidenecycloalkanone, respectively, which are valuable classes of intermediates in organic synthesis.

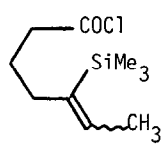
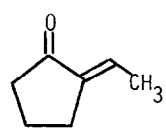
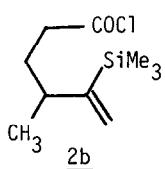
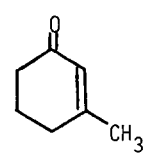
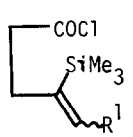
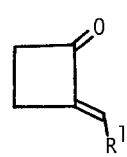
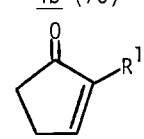
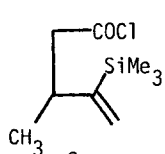
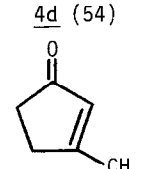
A recent publication[3] dealing with the cycloacylations of type A leading to cyclopentenones prompts us to disclose our own findings concerning the cycloacylations of type B. Herein we report that the intramolecular acylations of selected vinylic silanes (2, n = 1 and 2) afford the expected α-alkylideneketone (3) and/or the unexpected cycloenone (4), depending markedly upon the substitution pattern on the vinylsilane moiety and/or the chain length (n).



(1)

First of all, the availability of the starting acid (1) deserves special comment. In our continuing study on new synthetic applications of sigmatropic rearrangements, we have recently developed the sigmatropic variants of 2-(trimethylsilyl)allyl alcohol derivatives which provide facile entries to a variety of *functionalized* vinylsilanes including acids (1, n = 1 and 2).[4] Thus, the easy availability of acid 1 via the sigmatropic strategy strongly stimulated our interest in the present silicon-mediated cycloacylations.

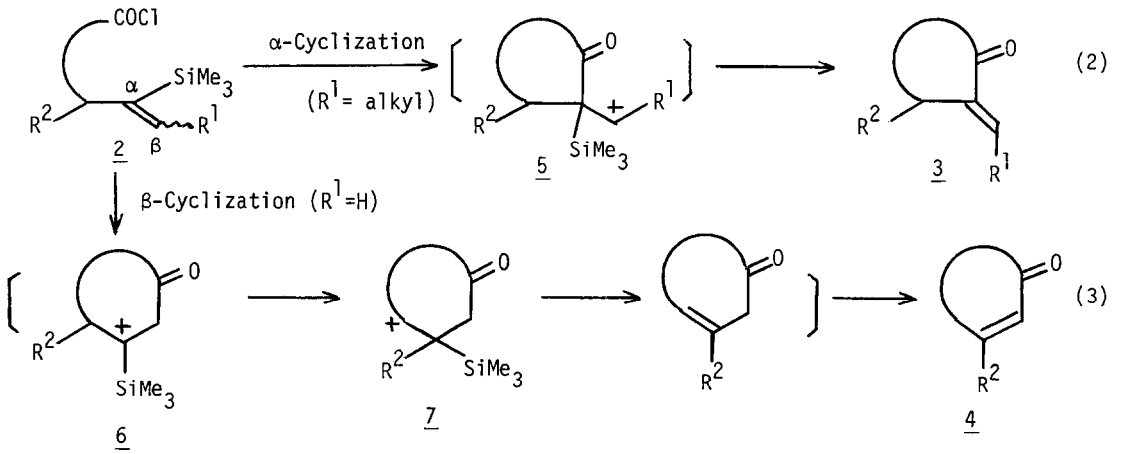
In this work we examined the internal acylations of the five acid chlorides (2a-e)[5] using aluminum chloride as the activator. Typically, chloride 2 was added to a dilute suspension of aluminum chloride (3 equiv) in dichloromethane (3 mmol/200 mL) at 0°C over a period of 3 h. The resulting mixture was stirred at 20-25°C for 10 h, hydrolyzed with aqueous $NaHCO_3$ at 0°C, and worked up as usual.[6] The cyclization products thus obtained are summarized in the table.

Entry	Substrate [E/Z]	Product 3[a](%Yield)[b]	Product 4[a](%Yield)[b]
1	 2a [80 : 20]	 3a (> 95) [E,> 95%]	
2	 2b		 4b (76)
3[c]	 2c, R^1=CH_3 [52 : 48] 2d, R^1= n-C_5H_{11} [55 : 42]	 3c (38) [E, > 95%] 3d (39) [E, > 95%]	 4c (62) 4d (54)
4	 2e		 4e (> 95)

[a] The spectral data (IR and NMR) of these products are fully consistent with the assigned structures including stereochemistry, if any. [b] Refers to isolated yields. [c] The two products were easily separated by column chromatography (silica gel, *n*-hexane/ether)

Inspection of the table reveals notable regiochemical trends in the present cycloacylations which are not necessarily consistent with the regiochemical rule ("β-effect")[7] widely accepted for the intermolecular versions. First, the most striking is that vinylsilane 2a gave the normal α-acylation product (3a),[8] whereas 2b afforded the unusual β-acylation product (4b), indicating that the substitution pattern on the vinylsilane moiety exerts a great influence in dictating product regiochemistry (*i.e.*, mode of cyclization). Second, comparison of entry 1 *vs.* 3 reveals that the regiochemical course is also affected, at least partially, by the chain length imposed between the acyl chloride and vinylsilane units. Third and more significantly, entries 2 and 4 obviously indicate occurrence of the migration of the methyl group at the allylic position during the unusual β-cycloacylation.

The observed regiochemistry (mode of cyclization), though rather ambiguous at first glance, may be clearly rationalized (or predicted) by appropriate considerations of the relative stability of the incipient cations and/or the ring strain involved. In the cycloacylations of vinylsilane possessing the β-alkyl substituent such as 2a, the secondary β-silylcarbenium ion (5) prevails as the incipient cation to give the normal α-cyclization product (3) (eq 2). In the cycloacylations of vinylsilanes without β-alkyl substituent such as 2b, on the other hand, the tertiary α-silyl cation (6) predominates over the primary β-silyl one (5, R^1=H),[9] ultimately leading to the unusual β-cyclization product (4) via the rearrangement of 6 to the β-silyl cation (7) (eq 3). In the cyclization of 2c or 2d, however, where the normal α-cyclization leading to the cyclobutanone (3c or 3d)[8] is depressed apparently by the large ring strain, the β-cyclization product (4c or 4d) is formed as the major product.



The regiochemical aspect outlined in this study not only offers the first example of the unprecedented β-(cyclo)acylation of vinylic silanes, but also suggests that one should not overestimate the "β-effect" in the electrophilic reactions of vinylic silanes in general. Furthermore, the present work coupled with our previous one[4] convincingly demonstrates the synthetic potential of the internal acylations of vinylic silanes for the construction of a variety of carbocyclic frameworks. We are now investigating different sets of intramolecular reactions of vinylic and allylic silanes easily available via our sigmatropic strategy.

Acknowledgment. This research was generously supported by the Kurata Foundation and the Grant-in-Aid for Scientific Research from Ministry of Education, Science, and Culture, Japan.

References and Notes

1. Review: E. W. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981.
2. For intramolecular alkylations of vinylic silanes, see: L. E. Overman and K. L. Bell, *J. Am. Chem. Soc.*, 103, 1851 (1981); B. M. Trost and E. Maruyama, *ibid.*, 103, 6529 (1981).
3. Recently an example of the cycloacylation of type A was reported: S. D. Burke, C. W. Murtiashaw, M. S. Dike, S. M. S. Strickland, and J. O. Saunders, *J. Org. Chem.*, 46, 2400 (1981). Professor I. Kuwajima of this Institute also examined a similar cycloacylation with a broad variety of vinylic silanes (a private communication).
4. K. Mikami, N. Kishi, and T. Nakai, *Chem. Lett.*, 1982, 1643.
5. Prepared in 60-88% distilled yields by treatment of acid 1 with oxalyl chloride.
6. This procedure is essentially the same as that used for the cycloacylation of acetylenic silanes: K. Utimoto, M. Tanaka, M. Kitani, and H. Nozaki, *Tetrahedron Lett.*, 1978, 2301.
7. For a pertinent discussion on β-effect, see: Chapter 3 of Colvin's book (ref 1). For specific exceptions to this generalization, see: I. Kuwajima, M. Kato, and T. Sato, *J. Chem. Soc., Chem. Commun.*, 1978, 478, and references cited therein.
8. The *E* geometry of 3a, 3c and 3d was unequivocally established through their NMR comparisons with those of the *E/Z* pair of an authentic sample or closely related compounds: J. E. Dubois and M. Dubois, *C. R. Acad. Sci., Ser. C*, 256, 715 (1963); M. Bertrand, R. Maurin, J. L. Gras, and G. Gill, *Tetrahedron*, 31, 849 (1975). The stereochemical aspect of the present cycloacylation will be discussed in a full paper.
9. While little has been known about the relative stability of tertiary α-silyl *vs.* primary β-silyl carbocation, the higher stability of the former is not entirely unexpected in view of the relatively weak electron-attracting effect of trimethylsilyl group linked to a π-system in general (*cf.* ref 8) and of the Kuwajima's finding in particular (ref 3) which implies that a tertiary (trialkyl) carbocation is more stable than even a secondary β-silyl cation. Overall, these considerations would suggest that, unless any steric restrictions are present, the relative stability of the carbocations concerned is in the order: tertiary trialkyl > secondary β-silyl > tertiary α-silyl > promary β-silyl.

(Received in Japan 15 November 1982)