Nitration of cyclic vinylsilanes with acetyl nitrate: effect of silyl moiety and ring size

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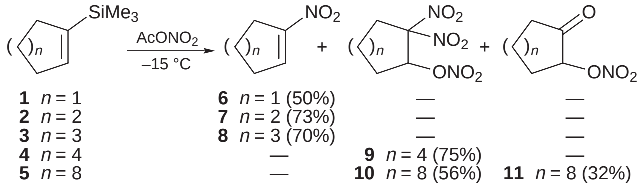
Reaction of $AcONO_2$ with common ring vinylsilanes gives the corresponding α,β-unsaturated 1-nitrocycloalkenes, and with medium and large ring vinylsilanes it produces novel 1,1-dinitro 2-nitrates.

The reaction of $AcONO_2$ with olefins leads to a plethora of products, which include isomeric nitro acetates, nitro nitrates and nitroalkenes.[1,2] However, the desired α,β-unsaturated nitroalkenes are obtained at best as only very minor products or not at all.[3] The results have been rationalized by proposing an oxazetidine intermediate, a [2 + 2] cycloadduct of a nitryl cation with an olefin.[1] Because of the well-known propensity of vinylsilanes to undergo regiospecific electrophilic substitution,[4] we considered that they could be nitrated[5] to the synthetically versatile α,β-unsaturated nitroalkenes.[6] This has now been realized in the case of common ring vinylsilanes. However, the medium and large ring vinylsilanes give different but interesting and novel products.

The nitration procedure is very simple. The cyclic vinylsilane (2.5 mmol) in CH_2Cl_2 (2 ml) at −15 °C was treated dropwise with $AcONO_2$[7] (5 mmol). After stirring the mixture for about half an hour (the disappearance of the vinylsilanes was monitored by GC), water was added and the mixture worked up in the usual manner. The products were purified by silica gel chromatography [2% EtOAc–light petroleum (bp 60–65 °C)].

For the present study, a series of 1-trimethylsilylcycloalkenes consisting of three common rings (**1**–**3**), one medium ring (**4**) and one large ring (**5**, a 1 : 1 mixture of *cis* and *trans* isomers) was employed.[8] The three common ring vinylsilanes **1**–**3** gave, in moderate to good isolated yields, the corresponding 1-nitrocycloalkenes **6**–**8** (Scheme 1), which were identical to authentic compounds.[3,5] No other products were detected in any of these cases.

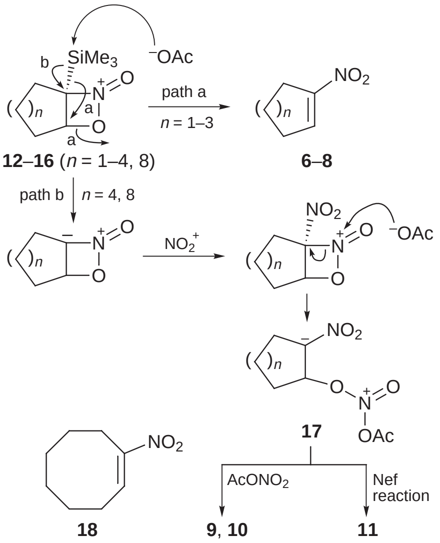


Scheme 1

1-Trimethylsilylcyclooctene **4** produced a single solid product, which was identified as 2,2-dinitrocyclooctyl nitrate **9**. 1-Trimethylsilylcyclododecene **5** (a 1 : 1 mixture of *cis* and *trans* isomers) gave a 2 : 1 mixture of the dinitro nitrate **10** and the keto nitrate **11** (Scheme 1), which were separated by repeated fractional crystallization from light petroleum (bp 60–65 °C). Compounds **9**–**11** were characterized by their spectral and elemental analysis data.[9] The expected 1-nitrocycloalkenes were not detected in either of these cases. This is in stark contrast to the results of nitration of cyclooctene, which was found to behave like the common ring cycloalkenes.[1]

The smooth conversion of the cyclic vinylsilanes **1**–**3** to the corresponding 1-nitrocycloalkenes **6**–**8** as the sole products is strikingly dissimilar to the complex results obtained in the nitration of their unsilylated analogues.[1] This clearly underlines the powerful influence of silicon in directing this transformation. The apparently different results from the medium and large ring vinylsilanes **4** and **5** can also be attributed to control by the silicon moiety.

All the results of $AcONO_2$ reaction with the cyclic vinylsilanes **1**–**5** can be rationalized by a mechanistic scheme involving the initial formation of a [2 + 2] cycloaddition intermediate **12**–**16** (Scheme 2), following the proposal of Borisenko *et al.* who based it on theoretical calculation and experimental results of $AcONO_2$ reaction with cycloalkenes.[1]



Scheme 2

In the present case, the regiospecificity is presumed to arise from the well-known β-silicon effect[4] which directs the electrophile NO_2^+ to attack the α position. Since the loss of silicon is more rapid than that of a β-proton in the β-elimination reactions of β-silicon-containing substrates, the further transformation of **12**–**16** is guided by this process. The β-elimination in **12**–**16** to the nitroolefinic products **6**–**8** occurs if silicon and the β-leaving group (C–O bond) attain the antiperiplanar geometry,[10] which is achieved when the carbocycles in **12**–**16** have the required conformation (*e.g.* cyclohexane in the chair form with α-C–$SiMe_3$ and β-C–O bonds being axial-axial *trans*). All the intermediates **12**–**16** from the vinylsilanes **1**–**5** can accommodate this conformational demand, but only those (**12**–**14**, n = 1–3) from the common ring vinylsilanes eventually lead to the 1-nitrocycloalkenes **6**–**8** (Scheme 2, path a). In the case of medium and large rings, the more rapid changes in their conformations and transannular interactions[10] probably diminish the life-time of the crucial conformation in which silicon and the leaving group are antiparallel to such an extent that the intermediate takes a different route to give the observed products (Scheme 2, path b).

We verified and confirmed that **9** is not formed from **4** *via* 1-nitrocyclooctene **18**. When **18**, prepared by a literature procedure,[11] was treated with $AcONO_2$ under conditions identical to those used for the nitration of **4**, the starting nitrocycloalkene **18** was recovered intact. We presume that the formation of **10** from **5** follows a similar route.

Additional evidence for this mechanistic scheme is the fact that no 1,2-nitro acetate, 1,2-nitro nitrate or transannular products are produced from any of the cyclic vinylsilanes **1–5**, unlike the reported results of the nitration of cycloalkenes under similar conditions.[1]

The formation of the keto nitrate **11** is likely to be due to a Nef-type transformation[12] of a possible intermediate **17**, which can also give the dinitro nitrate.

Our work demonstrates that nitration of cyclic vinylsilanes can be accomplished, though the nature of the products is dependent on the ring size, in that the common rings give the 1-nitrocycloalkenes and rings larger than seven-membered rings will produce novel dinitro nitrates.

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Notes and references

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9 *Selected data* for **9**: mp 56–58 °C; ν_{max}/cm^{-1} 1652, 1595, 1564; $\delta_H(CDCl_3)$ 6.19 (dd, *J* 7.6 and 1.4, 1H), 2.94–2.63 (m, 2H), 2.45–2.30 (m, 1H), 2.12–1.99 (m, 1H), 1.89–1.77 (m, 4H), 1.59–1.44 (m, 4H); $\delta_C(CDCl_3)$ 121.5 (s), 78.7 (d), 32.3 (t), 30.6 (t), 25.9 (t), 25.8 (t), 24.8 (t), 21.8 (t); $\delta_O(CDCl_3)$ 596.3, 445.2, 352.9; *m/z* 264 (1%, $M^+ + 1$), 171 (3), 95 (37), 81 (34), 67 (37), 55 (72), 46 (100, NO_2^+), 41 (67) (Found: C, 36.73; H, 5.03; N, 16.01. $C_8H_{13}N_3O_7$ requires: C, 36.51; H, 4.98; N, 15.96%). For **10**: mp 80–82 °C; ν_{max}/cm^{-1} 1667, 1595, 1569; $\delta_H(CDCl_3)$ 6.08 (d, *J* 9.9, 1H), 2.58–2.39 (m, 2H), 2.03–1.83 (m, 1H), 1.60–1.28 (m, 17H); $\delta_C(CDCl_3)$ 120.4, 74.9, 32.5, 26.6, 25.6, 25.0, 22.3, 22.1, 22.0, 21.8, 21.6, 19.6 (Found: C, 45.11; H, 6.81; N, 12.83. $C_{12}H_{21}N_3O_7$ requires: C, 45.14; H, 6.63; N, 13.16%). For **11**: mp. 89–91 °C; ν_{max}/cm^{-1} 1729, 1652, 1636; $\delta_H(CDCl_3)$ 5.29 (q, *J* 3.3, 1H), 2.81–2.71 (m, 1H), 2.50–2.40 (m, 1H), 2.14–1.85 (m, 3H), 1.64–0.88 (m, 15H); $\delta_C(CDCl_3)$ 204.3, 85.5, 34.8, 26.2, 26.1, 25.9, 23.7, 22.6, 22.2, 21.8, 21.0, 19.2 (Found: C, 59.05; H, 8.85; N, 5.38.$C_{12}H_{21}NO_4$ requires: C, 59.24; H, 8.70; N, 5.76%).

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