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THE REGIOCHEMISTRY OF THE (ETHOXYCARBONYL)NITRENE ADDITION REACTION TO SILOXYDIENES

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Summary. *1-Methoxy-3-methyl-1-siloxy-1,3-butadiene* **1** *adds (ethoxycarbonyl)nitrene generated by thermolysis to give the isomeric unsaturated amino esters* **4** *and* **7**; *under photolytic conditions the main products are the isomers* **4**, **5**, *and* **6**. *2-Trimethylsiloxyfuran* **8** *reacts with the same nitrene to give only* **10**, *either by thermolytic or photolytic route.*

1-Siloxy-1,3-dienes react with electrophiles in the alpha or the gamma position depending on the nature of the reagent[1] and/or as a function of temperature.[2] Carbenes, for example, give mainly addition to the double bond far from the siloxy group.[3]

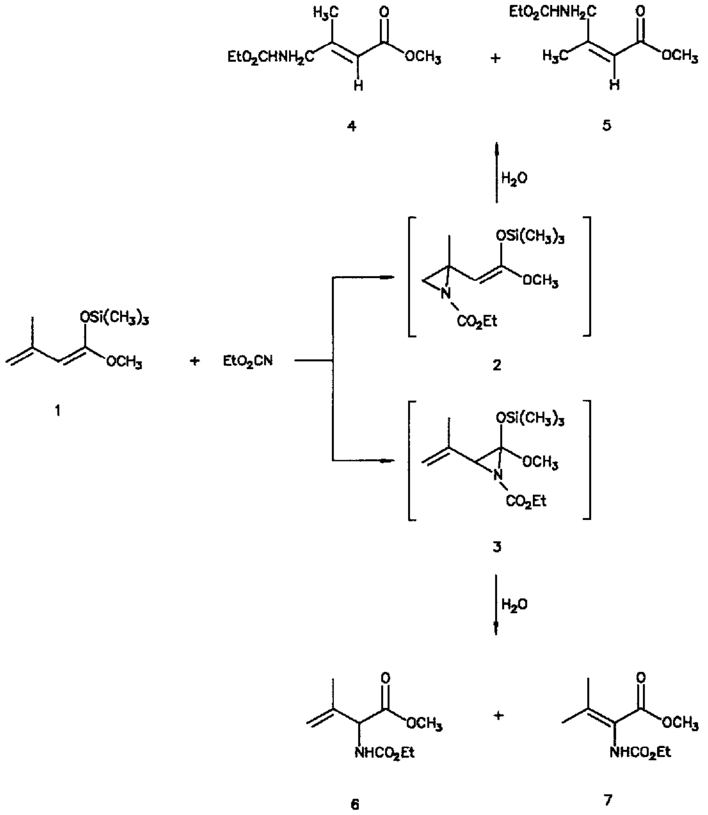
Our work on reactions between (ethoxycarbonyl)nitrene (EtO_2CN) and ethyl azidoformate (EtO_2CN_3) and silylated compounds such as enol silyl ethers and silyl ketene acetals showed that, under proper conditions, α-amino ketones[4] and α-amino esters[5] might be the main products.

Unsaturated α-amino acids being other interesting target molecules,[6,7] our attention was drawn to more unsaturated substrates containing the silyl ether group as possible precursors.

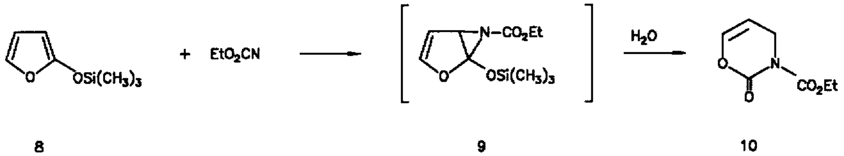
The addition reaction of EtO_2CN, generated from the thermolysis of *N,O*-bistrimethylsilyl-*N*-(ethoxycarbonyl)hydroxylamine,[8] to the siloxydiene **1**[9] gave a mixture of two isomeric products. Silica gel chromatography [petroleum ether (30-50 °C) - ethyl acetate, 9 : 1 v/v] allowed the purification of the products **4** and **7** (Scheme 1).

The photolysis of EtO_2CN_3 on the same substrate dissolved in dichloromethane at 0 °C produced a mixture of three isomeric products. The separation by chromatography as above gave the products **4**, **5**, and **6**. The structure of compounds **4**,[10] **5**,[11] **6**,[12] and **7**[13] was deduced by spectral data.

N-Substituted γ-amino esters (*E,Z* isomers) might be formed through the aziridine **2**, probably deriving from a formal 3,4-addition reaction, while the β,γ-unsaturated α-amino ester **6** and the isomeric α,β-unsaturated α-amino ester **7** likely seem to be the products of a formal 1,2-addition reaction giving the intermediate aziridine **3**. The conjugated unsaturated amino ester **7** might derive from a thermal isomerisation of the β,γ-unsaturated compound. Actually, a sample of **6** heated at 90 °C for 50 h, gave quantitatively **7**.



Scheme 1



Scheme 2

Only a slight preference for the formal 1,2-addition reaction is evident in both the photolysis and the thermolysis, with the exclusive formation of the more stable isomers in the latter case.

Table 1. Isolated yields of unsaturated *N*-substituted amino esters obtained by the reaction of siloxydiene **1** and EtO_2CN

product	thermolysis	photolysis
4	9	4.5
5	-	5
6	-	15
7	11.2	-

On the contrary, EtO_2CN generated under both the conditions above described adds to a cyclic siloxydiene such as siloxyfuran **8**[14] in a more selective way, giving only **10**,[15] in 34 % yield of separated product in the thermolysis and in 9 % in the photolysis, probably deriving from an unusual ring opening[16] of the intermediate aziridine **9** (Scheme 2).

This is not the only possible reaction path; the heteroaromatic compounds furan,[17] pyrrole,[17] and thiophene[17,18] add EtO_2CN giving products of a different rearrangement.

It is noteworthy that the same masked butenolide **8** undergoes addition by carbon electrophiles in the gamma position.[19]

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10. IR (CCl_4) 3465, 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (1H, s), 4.85 (1H, s), 4.13 (2H, q), 3.83 (2H, d), 3.70 (3H, s), 2.13 (3H, s), 1.25 (3H, t); *m/z* 201 (9 %), 96 (100 %).
11. IR (CCl_4) 3460, 1730, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.77 (1H, s) 5.38 (1H, s), 4.19 (2H, d), 4.11 (2H, q), 3.70 (3H, s), 1.99 (3H, s), 1.25 (3H, t); *m/z* 201 (10 %), 96 (100 %).
12. IR (CCl_4) 3450, 1730, 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53 (1H, s), 5.03 (1H, s), 4.98 (1H, s), 4.77 (1H, d), 4.08 (2H, q), 3.72 (3H, s), 1.74 (3H, s), 1.20 (3H, t); *m/z* 201 (2 %), 142 (100 %).
13. IR (CCl_4) 3450, 1730, 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.86 (1H, s), 4.15 (2H, q), 3.75 (3H, s), 2.15 (3H, s), 1.88 (3H, s), 1.25 (3H, t); *m/z* 201 (9 %), 68 (100 %).
14. Commercially available (Fluka).
15. IR (CCl_4) 1785, 1750, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.58 (1H, dt), 6.16 (1H, dt), 4.90 (2H, t), 4.19 (2H, q), 1.25 (3H, t).
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