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OXAZINONE VERSUS ALLENE FORMATION IN THE REACTION OF N-ALKOXYCARBONYLIMINIUM IONS WITH PROPARGYLTRIMETHYLSILANE

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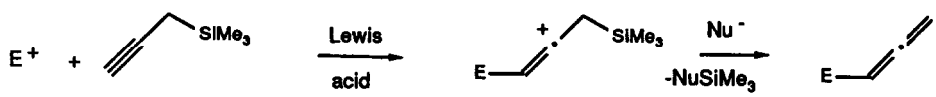
Abstract: Reactions of N-alkoxycarbonyliminium ions with propargyltrimethylsilane, promoted by Lewis acid, yield in most cases mixtures of allenes G and oxazinones H.

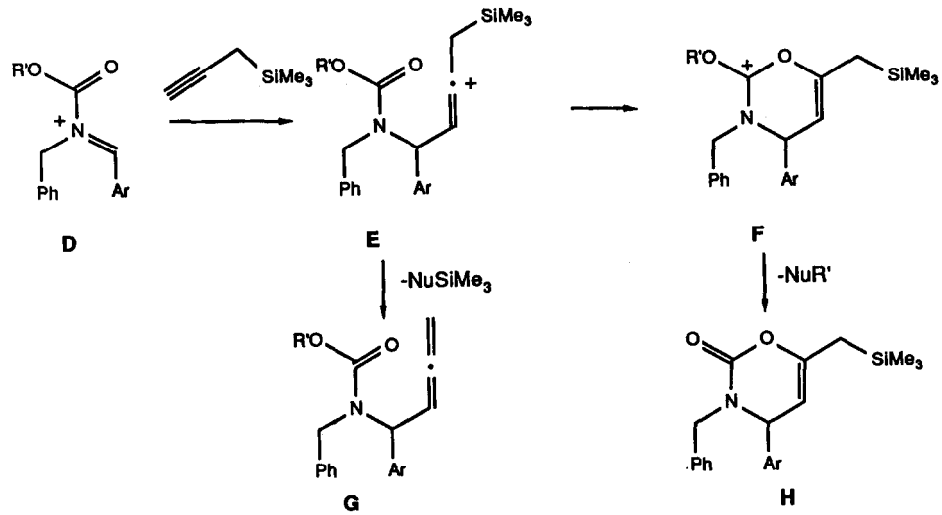
In recent years, propargyltrimethylsilane (A) has been shown to be a useful starting material for the synthesis of monosubstituted allenes C. In the presence of a Lewis acid, silane A reacts with various electrophiles E^+, such as protons[1], acid chlorides[2], acetals[3], aldehydes[4,5], ketones[5,6], Michael acceptors[6], and N-acyliminium ions[7]. These reactions are characterized by a propargyl-allenyl rearrangement, which proceeds through the intermediacy of a vinylic carbocation B, stabilized by a β-silicon atom[8]. We have investigated the utility of N-alkoxycarbonyliminium ions D as electrophiles in this process, as a possible route to the pharmacologically interesting α–allenic amines[9]. We herewith report results, which show that iminium ions D do not give good yields of allenes G, but mainly lead to oxazinones H by way of F, as a consequence of intramolecular trapping of the vinylic cation E.



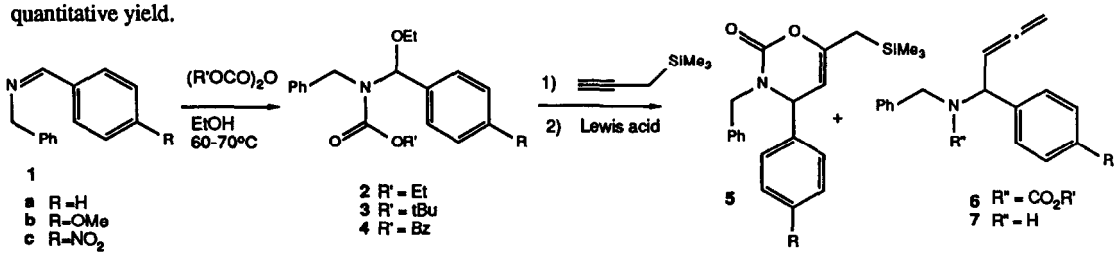
A B C

The carbamates **2a**, **2b**, **2c**, **3b** and **4b** (see Table) were utilized as precursors to the required iminium ions D. These precursors were synthesized by reaction of Schiff bases **1a**, **1b** and **1c** with the appropriate, commercially available, pyrocarbonates $(R'OCO)_2O$ as shown in the Table[10]. Yields were good, except for the *p*-nitrophenyl substituted imine **1c**, which reacted very slowly, due to the lower nucleophilicity of the imine nitrogen.

A mixture of carbamate **2a** and propargyltrimethylsilane[6] (3 equiv) in dichloromethane was treated with tin tetrachloride (1.2 equiv) for 0.5 hr at 0°C, followed by 2 hr at 20°C. The reaction mixture was poured out into saturated aqueous sodium bicarbonate and extracted with chloroform. Flash chromatography of the crude product[11] furnished the 3,4-dihydro-2*H*-1,3-oxazin-2-one **5a**[12] in 48% yield (Table, entry 1). The expected allene **6a** could not be detected. However, when ethylaluminium dichloride was used as Lewis acid in benzene, the allene **6a**[12] was formed as the major product (Table, entry 2). The carbamates **2b**, **3b** and **4b** gave similar results as **2a**, as shown in the Table (entries 3 to 6). The oxazinone **5b**[12] was the major or exclusive product in all cases. Carbamate **2c** (Table, entry 7) gave a low yield of oxazinone **5c**[12] (10%), most likely due to very slow formation of the iminium ion, which is destabilized by the *p*-nitro function.



The above results can be rationalized by invoking the vinylic carbocation **E** as intermediate. This ion can either loose the trimethylsilyl group to form allene **G**, or cyclize, by way of reaction with the carbonyl group, to produce intermediate **F**, and hence oxazinone **H**.[13,14] The formation of **G** renders a concerted $[\pi 4_s + \pi 2_s]$-cycloaddition mechanism[15] for the formation of **F** from **D** unlikely. The significance of **E** as intermediate is confirmed by the fact that 1-pentyne (lacking the β-cation stabilizing silicon substituent) did not react with **2b** under the same conditions. It is furthermore interesting to note that reaction of **2b** with allyltrimethylsilane led to the expected **12**[12] in virtually quantitative yield.

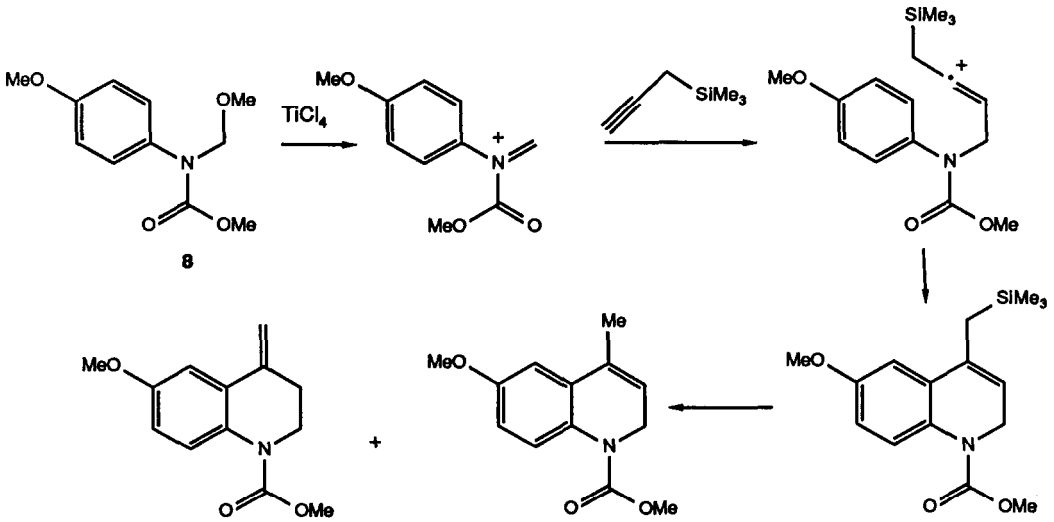


entry		equiv[a]	time (hrs)		yield[b] (%)	solvent	Lewis acid	ratio oxazinone/allene[d]				yield[b] (%)
1	**1a**	1.2	24	**2a**	85	CH_2Cl_2	$SnCl_4$	**5a**	100		0	48
2						C_6H_6	$EtAlCl_2$	**5a**	34	**6a**	66	45[e]
3	**1b**	1.2	17	**2b**	84	CH_2Cl_2	$SnCl_4$	**5b**	100		0	56
4						CH_2Cl_2	$SnCl_4$	**5b**	75	**6b**	25	63[e]
5		2.0	24	**3b**	80	CH_2Cl_2	$EtAlCl_2$	**5b**	100		0	67
6		1.2	24	**4b**	55	CH_2Cl_2	$EtAlCl_2$	**5b**	80	**7**	20	50
7	**1c**	2.2	48	**2c**	51[c]	CH_2Cl_2	$SnCl_4$	**5c**	100		0	10

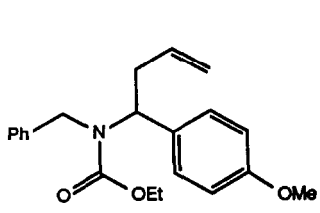
a) of pyrocarbonate; b) after flash chromatography; c) incomplete reaction; d) by ^1H NMR integration; e) **5** and **6** could not be separated by flash chromatography

Table

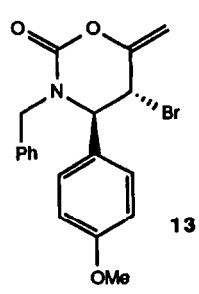
As a structural modification of the above type of iminium ion precursor we synthesized carbamate **8** from p-anisidine (a. MeO_2CCl, pyridine, 90% ; b. NaH, $ClCH_2OMe$, DMF, 88%). To our surprise, reaction of **8** with propargyltrimethylsilane (3 equiv, 1.2 equiv $TiCl_4$, CH_2Cl_2, 0^0 to 20^0C) furnished a 3:1 mixture of double bond isomers **10**[12] and **11**[12] in 44% yield. This outcome shows that the N-*p*-methoxyphenyl function successfully competes with the carbamate function in trapping the vinylic carbocation. Apparently, the allylsilane **9** is not stable under the reaction conditions since only the protodesilylation products were isolated.



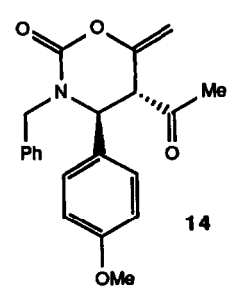
Finally, we investigated the chemical properties of oxazinone **5b** in some detail. It is surprising that this type of compound which is both an allylsilane and an enol derivative[16] survived the reaction conditions of its formation. Yet, **5b** reacted as a normal allylsilane with bromine and acetyl chloride. Reaction with bromine at -20^0C in carbon tetrachloride gave bromide **13**[12] in 73% yield as a crystalline solid (mp 130-131^{0}C). Acetyl chloride reacted with **5b** in the presence of aluminium chloride in dichloromethane at -78^0C to produce **14**[12] in 58% yield. Both compounds were formed as pure trans stereoisomers, which showed very small coupling constants (1.5 Hz) between the ring hydrogens. The structure of **13** was proved by an X-ray crystallographic analysis (see Figure).[17]



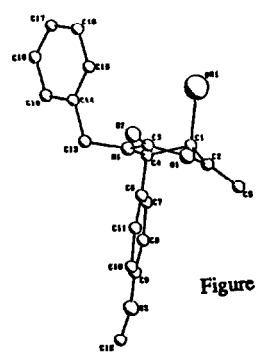
12



13



14



Figure

Acknowledgements: We are grateful to Mr. K. Goubitz and Mr. D. Heijdenrijk of the Laboratory of Crystallography for performing the X-ray analysis. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

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11. The major by-product was ethyl N-benzylcarbamate, which results from hydrolysis of **2a**.
12. This compound showed spectra (^{1}H NMR, ^{13}C NMR, IR) and high resolution mass data in accord with its structure.
13. The interception of carbocationic intermediates by the carbamate carbonyl group is well-known: P.A. Bartlett, D.J. Tanzella, J.F. Barstow, *Tetrahedron Lett.* **23**, 619 (1982); Y-F. Wang, T. Izawa, S. Kobayashi, M. Ohno, *J. Am Chem. Soc.* **104**, 6465 (1982); S. Knapp, D.V. Patel, *Tetrahedron Lett.* **23**, 3539 (1982); M. Mühlstädt, B. Olk, R. Widera, *Tetrahedron Lett.* **24**, 3979 (1983); Y. Yamamoto, T. Komatsu, K. Maruyama, *J.Org.Chem.* **50**, 3115 (1985).
14. For related results from allenyl- and vinylsilanes see, respectively, R.L. Danheiser, C.A. Kwasigroch, Y-M. Tsai, *J.Am.Chem.Soc.* **107**, 7233 (1985) and C. Angst, *Pure Appl.Chem.* **59**, 373 (1987).
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16. Such compounds are rare; for some recent examples see: H. Kleijn, P. Vermeer, *J.Org.Chem.* **50**, 5143 (1985).
17. Details of this structure determination will be published elsewhere.
18. Some selected spectral data are: **5a**: ^{1}H NMR (C_6D_6) δ 0.00 (s, 9H, $SiMe_3$), 1.36 (s, 2H, CH_2Si), 3.46 and 5.38 (AB system, 2H, *J*= 15 Hz, CH_2Ph), 4.22 (m, 1H), 4.47 (m, 1H), 6.8-7.3 (m, 10H); ^{13}C NMR (C_6D_6) δ −1.5, 22.8, 49.1, 58.9, 97.9, 127.1, 127.8, 128.3, 128.4, 128.9, 129.2, 136.9, 141.7, 149.2, 150.8; IR (cm^{-1}, $CHCl_3$) 1710 (C=O), 1245, 850 (Si-C). **5b**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H, $SiMe_3$), 1.60 (s, 2H, CH_2Si), 3.56 and 5.21 (AB system, 2H, *J*= 15 Hz, CH_2Ph), 3.81 (s, 3H, OMe), 4.59 (s, 2H, CHN, -CH=), 6.8-7.4 (m, 9H); ^{13}C NMR ($CDCl_3$) δ −1.6, 22.5, 48.4, 55.2, 57.7, 97.6, 114.2, 127.5, 128.0, 128.2, 128.5, 135.8, 148.5, 150.9, 159.5, 162.6. **6a**: ^{1}H NMR ($CDCl_3$) δ 1.14 (t, 3H, *J*= 7 Hz), 4.14 (q, 2H, *J*= 7 Hz), 4.22 and 4.53 (AB system, 2H, *J*= 16 Hz, CH_2Ph), 4.75 (dd, 2H, *J*= 2, 7 Hz, $=CH_2$), 5.42 (q, 1H, *J*= 7 Hz, -CH=), 5.80 (m, 1H, NCH), 7.0-7.5 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.5, 48.9, 59.3, 61.5, 76.9, 89.7, 126.7, 127.4, 127.7, 128.1, 128.3, 138.8, 139.5, 156.8, 209.0; IR(cm^{-1}, $CHCl_3$) 1955 (=•=), 1685 (C=O). **7**: ^{1}H NMR ($CDCl_3$) δ 1.81 (s, 1H, NH), 3.75 (s, 2H, $PhCH_2$), 3.79 (s, 3H, OMe), 4.23 (dt, 1H, *J*= 2, 7 Hz, NCH), 4.80 (dd, 2H, *J*= 2, 6 Hz, $=CH_2$), 5.25 (q, 1H, *J*= 6 Hz, -CH=); ^{13}C NMR ($CDCl_3$) δ 51.3, 55.2, 60.3, 76.9, 94.6, 113.9, 126.9, 128.2, 128.3, 128.4, 135.1, 140.3, 158.9, 207.6; IR (cm^{-1}, $CHCl_3$) 3300 (NH), 2830 (OMe), 1950 (=•=). **12**: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3H, *J*= 7 Hz, OCH_2CH_3), 2.62 (m, 2H, CH_2CH=), 3.76 (s, 3H, OMe), 4.08 and 4.40 (AB system, 2H, *J*= 16 Hz, CH_2Ph), 4.17 (q, 2H, *J*= 7 Hz, OCH_2CH_3), 4.85-5.10 (m, 2H, $=CH_2$, 5.34 (bt, 1H, *J*= 8 Hz, NCH), 5.45-5.95 (m, 1H, -CH=), 6.75-7.35 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 14.5, 36.0, 47.3, 55.0, 58.7, 61.2, 113.6, 116.9, 126.5, 127.4, 127.9, 129.3, 131.5, 134.9, 139.1, 156.8, 158.9; IR (cm^{-1}, $CHCl_3$) 2840 (OMe), 1680 (C=O). **13**: ^{1}H NMR ($CDCl_3$) δ 3.71 and 5.27 (AB system, 2H, *J*= 14 Hz, CH_2Ph), 3.80 (s, 3H, OMe), 4.31 (d, 1H, *J*= 2 Hz, =CH), 4.47 (d, 1H, *J*= 1.5 Hz), 4.53 (d, 1H, *J*= 1.5 Hz), 4.78 (d, 1H, *J*= 2 Hz, =CH), 6.75-7.4 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 43.6, 50.9, 55.2, 63.7, 97.2, 114.5, 127.6, 127.9, 128.3, 128.4, 128.9, 134.8, 149.4, 149.5, 160.1; IR (cm^{-1}, $CHCl_3$) 2840 (OMe), 1725 (C=O), 1655 (C=C). **14**: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H, COMe), 3.27 (d, 1H, *J*= 1.5 Hz, CHAc), 3.76 and 5.05 (AB system, 2H, *J*= 15 Hz, CH_2Ph), 3.78 (s, 3H, OMe), 4.31 (d, 1H, *J*= 2 Hz, =CH), 4.76 (d, 1H, *J*= 1.5 Hz, NCH), 4.95 (d, 1H, *J*= 2 Hz, =CH), 6.75-7.4 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 27.2, 50.9, 55.1, 56.2, 57.3, 98.8, 114.2, 127.4, 127.7, 128.2, 128.7, 129.8, 135.2, 148.9, 150.2, 159,5, 194.8; IR (cm^{-1}, $CHCl_3$) 2840 (OMe), 1720 (C=O), 1660 (C=C).

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