A NOVEL SYNTHESIS OF TRIALKYLSTANNYL- AND SILYLPYRIDINE DERIVATIVES THROUGH DIELS-ALDER REACTION OF 6*H*-1,3-OXAZIN-6-ONES[1]

Yutaka Yamamoto * and Yasuo Morita

Tohoku College of Pharmacy
4-4-1 Komatsushima, Aoba-ku, Sendai 981, Japan

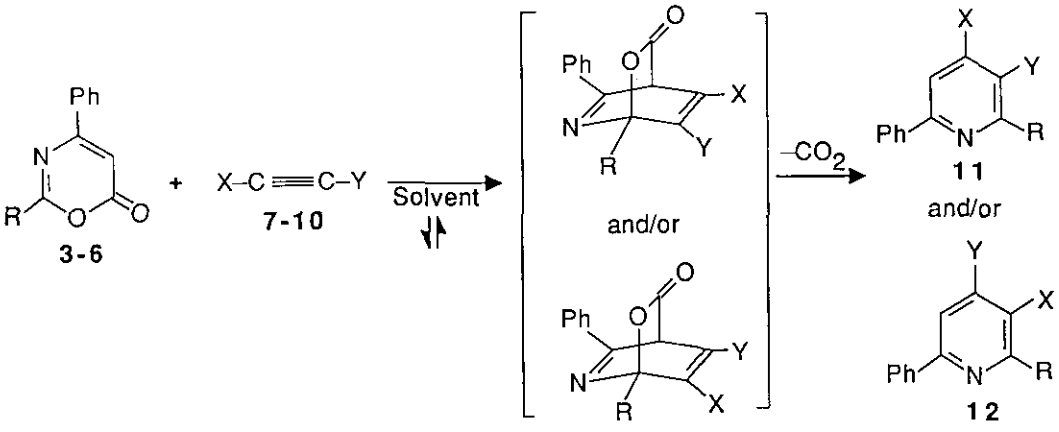
Abstract --- A novel and convenient method for the synthesis of trimethylstannyl- and silylpyridine derivatives through Diels-Alder reaction of 6*H*-1,3-oxazin-6-ones with trialkylstannyl- and -silylacetylene derivatives was developed.

A number of reports concerning with the use of organostannyl group as a useful synthetic tool in heterocyclic chemistry have recently been accumulated.[2] From this laboratory, carbon-carbon bond formation on electron deficient ring system *via* the organostannyl derivative has been shown ; preparation of pyridyl ketones from trimethylstannylpyridines (**1**)[3] and acyl chlorides, and palladium catalyzed cross-coupling reactions of **1** with vinyl,[4] allyl,[4] aryl,[5] and heteroaryl halides.[5]

Recently, attention has increasingly focused on 6*H*-1,3-oxazin-6-one derivatives **2** from a view of participation in inverse electron demand Diels-Alder reaction.[6] We reported a general method for synthesis of **2** from imino ethers and Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione).[7] We wish to report in this communication a novel and facile synthesis of trialkylstannylpyridines along with trialkylsilylpyridines by [4+2] cycloaddition of **2** with organostannyl- and -silylacetylene compounds.

The reactions of 1,3-oxazin-6-ones **3**-**6** with bis(trimethylstannyl)acetylene (**7**) or tributylstannylacetylene (**8**) were carried out in the following general procedure ; a mixture of **3**-**6** (5 mmol) and **7** or **8** (10 mmol) in dibutyl ether (10 ml) was refluxed for the period indicated in Table, followed by chromatographic separation. When monosubstituted stannylacetylene **8** was used as a dienophile, 4-tributylstannylpyridine derivatives **11** were obtained as a major product together with 3-tributylstannylpyridines **12**. The results are summarized in Table.

This paper is dedicated to the late Professor Tetsuji Kametani.



Scheme

Table. Preparation of bis(trimethylstannyl)pyridines **11a-d**, tributylstannylpyridines **11e-h**, **12e-h**, bis(trimethylsilyl)pyridines **11i-k**, and trimethylsilylpyridines **11l-n**, **12m**.[8]

	1,3-oxazin-6-one		dienophile			reaction conditions			yield(%)	
entry	R		X	Y		solvent[a]	time(h)		**11**	**12**
1	Me	**3**	Me_3Sn	Me_3Sn	**7**	A	21	**a**	20	
2	Ph	**4**			**7**	A	21	**b**	40	
3	H	**5**			**7**	A	3.5	**c**	71	
4	CO_2Et	**6**			**7**	A	13	**d**	69	
5	Me	**3**	Bu_3Sn	H	**8**	A	48	**e**	36	4
6	Ph	**4**			**8**	A	17	**f**	32	15
7	H	**5**			**8**	A	8.5	**g**	51	18
8	CO_2Et	**6**			**8**	A	20	**h**	46	17
9	Me	**3**	Me_3Si	Me_3Si	**9**	B	120	**i**	40	
10	H	**5**			**9**	B	54	**j**	79	
11	CO_2Et	**6**			**9**	B	116	**k**	88	
12	Me	**3**	Me_3Si	H	**10**	B	64	**l**	61	
13	H	**5**			**10**	B	48	**m**	38	28
14	CO_2Et	**6**			**10**	B	62	**n**	81	

a) A : Dibutyl ether, B : Decalin.

In these reactions, the ease of the cycloaddition might be depend on the substituent at the 2-position of the oxazine ring. Thus, 2,4-disubstituted (alkyl or aryl) oxazines (Table, entries 1,2,5 and 6)require longer reaction time and the yields are relatively low. In contrast, 2-unsubstituted oxaizne **5** (Table, entries 3 and 7) was found to react with **7** or **8** smoothly to give stannylpyridines **11,12** in fairly good yield. Electron withdrawing substituents on the 2-position of the oxazine ring (Table, entries 4 and 8) also accelerates the reaction rate and raise the yield of stannylpyridines **11,12**.

Further, the reaction of 1,3-oxazines **3-6** with bis(trimethylsilyl)acetylene (**9**) or trimethylsilylacetylene (**10**) led to the formation of trimethylsilylpyridines **11, 12**. The results are also summarized in Table. In these reactions, the use of dibutyl ether gave no product and decalin was used instead of dibutyl ether as a solvent. The effects of the substituent on the 2-position of the oxazine ring are similar to the reaction of stannylacetylenes **7, 8** with oxazines **3-6**.

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8. All compounds exhibited ir and nmr data in full accord with their structure and gave satisfactory microanalysis.

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