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UNSATURATED GERMANES AND STANNANES IN THE SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLES BY [2+3]-CYCLOADDITION*

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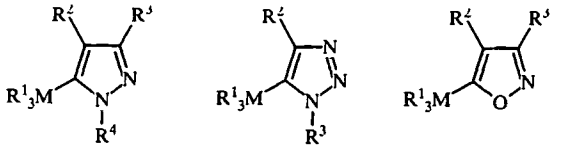
Literature data and the results of fundamental investigations on synthetic methods and chemical reactions of the products of 1,3-dipolar additions to unsaturated germanes and stannanes are reviewed.

Alkenylgermanes and stannanes are of interest as model substances for the study of the effect of organometallic substituents on the reactivity of multiple bonds and as valuable synthons in organic synthesis. Because of their $(p\text{-}d)\pi$ interactions, vinylgermanes differ from their carbon analogs in nucleophilic and electrophilic addition reactions. Allylgermanes in their turn are more nucleophilic than vinylgermanes and the corresponding carbon analogs.

Only when the multiple bond is separated from the germyl substituent by two or more carbon atoms is the reactivity comparable to the corresponding alkene in reactivity. Note that unsaturated germanes and stannanes are valuable and promising intermediates in organic synthesis.

1,3-Dipolar addition to unsaturated silanes is a very valuable method for the synthesis of nitrogen-containing heterocycles which has been thoroughly studied and reviewed [1, 2]. However, there has been little unsystematic study of the analogous reactions in organogermanium and organotin chemistry. [2+3]-Dipolar addition has been used in the synthesis in organometallic substituted pyrazoles (I), triazoles (II) and isoxazoles (III).



I II III

Preparative methods for and the chemical properties of compounds I-III are discussed in this review.

1. SYNTHETIC METHODS

1.1. Cycloaddition of Diazoderivatives

A general method for the synthesis of pyrazole derivatives of germane and tin is the reaction of diazo compounds to germyl(stannyl)acetylenes. Germyl(stannyl)acetylene undergoes cycloaddition with diazomethane in absolute ether [3-5]. Diazomethane adds to germyl- or stannylacetylene to pyrazoles with germyl or stannyl substituents at position 3 of the heterocycle which indicates that the β-carbon atom of the triple bond is more electrophilic than the α-carbon atom at the moment of reaction. The terminal nitrogen atom of diazomethane adds to the more substituted carbon atom of the triple bond (Table 1).

*Dedicated to Professor A. Katritzky on his seventieth birthday.

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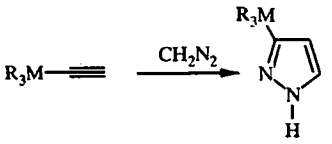
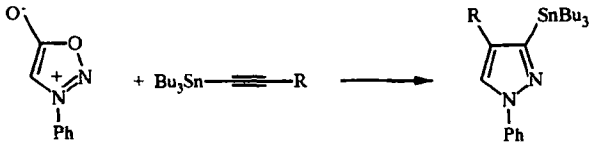


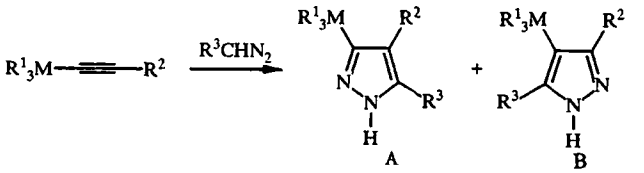
Ia-f

Table 1 shows that the reactivity of the acetylenes with respect to reaction with diazomethane decreases in the order Ge > Sn > Pb.

The [2+3]-cycloaddition of the betaine 3-phenyl-1,2,3-oxadiazol-5-onium (3-phenylsydnone) [6] to ethynyltributylstannane and bistributylstannylacetylene proceeds in high yield in boiling xylene to give 3-tributylstannyl-1-phenylpyrazole (85%) and 3,4- bis(tributylstannyl)-1-phenylpyrazole (100%) respectively [7]. The alternative method, synthesis of stannylpyrazoles by metallation of pyrazole with butyl lithium with subsequent reaction with chlorotributylstannane, was less successful because of low yield of products [8].

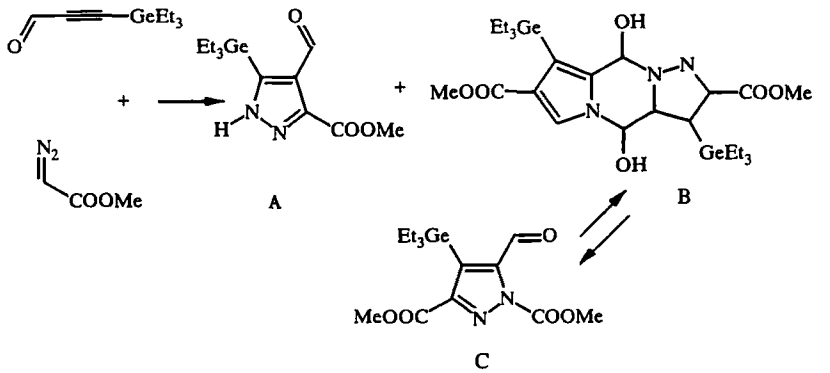


β-Substituted ethynylgermanes and stannanes undergo [2+3]-cycloaddition with diazo compounds to give mainly a mixture of regioisomers [9-11]. To prevent nitrogen elimination the reaction is carried out in absolute ether at room temperature in the dark. The reaction with diazomethane occurred under the mildest conditions (one week at −70°C, otherwise at 0°C). The reactions with diazomethane and ethyl diazoacetate occurred quantitatively, while the yield with diazoacetone was 51%. In no case was the reaction regioselective: a mixture of isomers was formed.

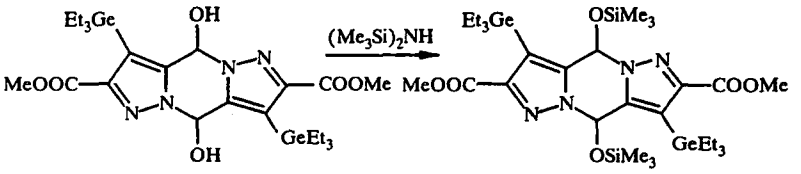


2a-i

1-3-Dipolar addition of diazomethane to the triple bond of ethynylgermanes and stannanes (2a, b, f, g) occurs regioselectively to give isomer A. Reaction with ethyl diazoacetate and diazoacetone gave a mixture of the isomeric pyrazoles A and B, the ratio depending on the structure of the 1,3-dipole. The reaction of 1-triethylgermyl-1-propyn-3-al with methyl diazoacetate in ether at room temperature was unusual [12, 13]. Under these conditions the cyclic hemiaminal B was formed along with the formylpyrazole. Compound B was in equilibrium with pyrazole C in solution.

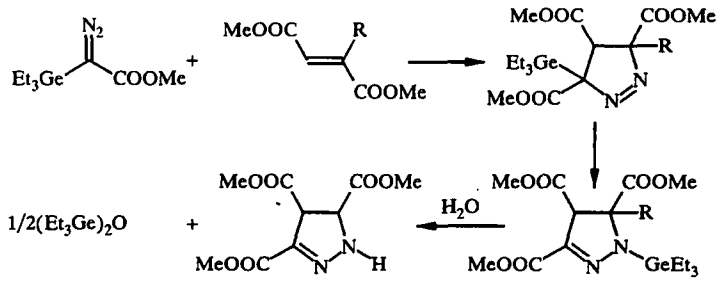


Dimer B was converted quantitatively into the bistrimethylsilyl ether D on treatment with an excess of hexamethyldisilazane in THF.



Metallated pyrazole aldehydes with an unsubstituted nitrogen atom next to the ring carbon atom bonded to the aldehyde group exist as the dimer B in the solid state. In solution, dimerization is reversed and the position of equilibrium depends on the solvent and the temperature. Polar solvents (methanol, DMSO, HMPT) bond to the reactive C=O or NH centers, which facilitates shift of the equilibrium towards the formylpyrazole.

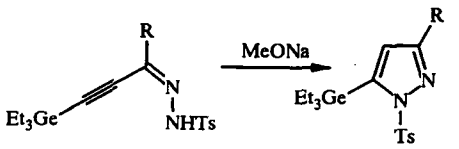
[2+3]-Dipolar cycloaddition of methyl triethylgermyldiazoacetate to dimethyl fumarate and dimethyl 1-triethylgermyl-1,2-ethylenedicarboxylate gave Δ_1-pyrazolines [14]. As a result of 1,3-migration of the triethylgermyl group, the monogermyl adduct isomerized to the Δ_2-pyrazoline which is easily hydrolyzed at the Ge−N bond to give hexaethyldigermoxane and 3,4,5-trimethoxycarbonyl-2-pyrazoline (78%).



R = H, Et_3Ge

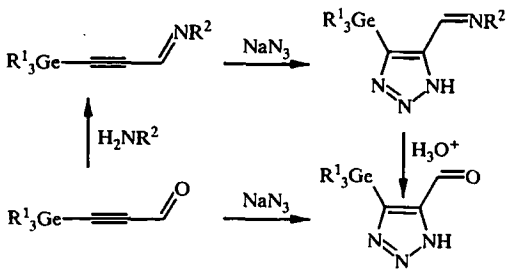
In contrast, the digermyl product is not hydrolyzed under comparable conditions and does not contain an N−H bond either before or after treatment with water according to the IR spectra. Probably the pyrazoline is less labile and does not undergo reaction. Note that the esters were mixtures of isomers and consequently the products are mixtures of isomeric Δ_1-pyrazolines.

One known method for the synthesis of diazo compounds is based on the reaction of ketone tosylhydrazones (including organosilicon examples) with alkali metal alkoxides [15]. However, the tosylhydrazones of germylacetylenic carbonyls in the presence of sodium ethoxide in pyridine at 50-60°C cyclize to the corresponding tosylpyrazoles in 40-55% yield.

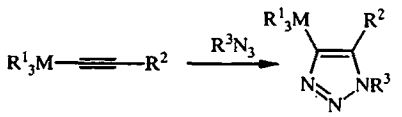


1.2. Cycloaddition of Azides

Depending on the direction of the reaction — at the double or triple bond in germylaldimines - addition of 1,3-dipolar reagents may form compounds with different structures, containing active triorganogermyl, ethynyl and azomethine fragments capable of undergoing chemical reactions [16]. For example, it was established that after treatment of the reaction mixture from the reaction of aldimines with sodium azide with acidified water the only products were 4-trialkylgermyl-1,2,3-triazol-5-carbaldehydes which suggests initial addition of the azide at the triple bond, demetallation of the corresponding sodium salt and hydrolysis of the azomethine group. The possible splitting of the Ge−C_{sp} bond during the reaction of the germanyl aldimine did not occur.



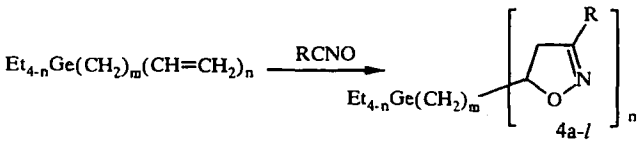
Germanium containing aldimines [17], aminoethynylgermanes and stannanes [18] add phenyl, *p*-methoxyphenyl, *p*-nitrophenyl and sulfo azides with the same chemo- and regioselectivity, but under considerably more vigorous conditions, to give the corresponding 1,2,3-triazoles. The direction of addition to trialkylgermyl-1-aza-1-buten-3-ine did not depend on the structure of the substituent at germanium, the aldimine or the azide. The reactivity of the azide increased clearly with increased nucleophilicity in the series R^3: Na > Ac [19] > H [20] > phosphoryl [21] > 4-$MeOC_6H_4$ > Ph > 4-$NO_2C_6H_4$ [21] > alkyl [19] and the reactivity decreased somewhat in dependence on the electron donating properties of the substituents at the triple bond in the order Me_3Ge > Me_3Sn > Me_3C.



3a-j

1.3. Cycloaddition of Nitrile Oxides

The [2+3]-dipolar addition of nitrile oxides to vinylsilanes proceeds regioselectively to give 5-silicon substituted isoxazoline-2 derivatives [22-25]. Exceptions are additions to triethoxyvinyl silane and vinylsilatrane in which 4-silicon substituted isoxazolines are formed together with the 5-isomer [26]. Vinyl- and allyltriethylgermane and diethyldivinylgermane undergo cycloaddition with nitrile oxides actively to give corresponding 5-germyl substituted isoxazoline-2 derivatives regiospecifically in good yield (42-73%) [27-30]:



4a-*l*

The nitrile oxides were prepared *in situ* as follows: 1) from primary nitroalkanes in the presence of phenyl isocyanate and a catalytic amount of triethylamine; 2) from hydroxamic acid chlorides in the presence of a base as hydrogen chloride acceptor.

The first method was used to obtain 3-methyl-5-germyl substituted isoxazolines. The reaction was carried out in benzene, with dropwise addition of nitroethane with a catalytic amount of triethylamine to a mixture of the alkenylgermane and two equivalents of phenyl isocyanate. The beginning of the reaction was signaled by the beginning of CO_2 evolution and the precipitation of diphenylurea. The rate determining step is addition of the nitrile oxide to the germylalkene so it is very important to add the nitroethane slowly to avoid the dimerization reaction which gives furoxan.

A natural inconvenience of the second method is chlorination of the aldoximes. Chlorination of benzaldoximes is often accompanied by the side reaction of chlorination of the aromatic ring, but the side reaction does not occur if N-chlorosuccini-

TABLE 1. Cycloaddition of Diazomethane to Germyl(stannyl)acetylene

Compound	M	R	Reaction time, h	Temperature, °C	Yield, %
Ia	Ge	Me	4	30	100
Ib	Ge	Ph	6	95	100
Ic	Sn	Me	4	20	71
Id	Sn	Pr	6	34	68
Ie	Sn	Ph	6	80	100
If	Pb	Ph	6	75	65

TABLE 2. Cycloaddition of Diazo Compounds to β-Substituted Ethynylgermanes(stannanes)

Compound	M	R^1	R^2	R^3	Yield, %	
					A	B
2a	Ge	Me	OEt	H	95	-
2b	Ge	Et	OMe	H	94	-
2c	Ge	Et	COMe	H	50	49
2d	Ge	Et	COMe	COOMe	18	73
2e	Ge	Et	COMe	MeCO	31	20
2f	Sn	Me	OEt	H	91	-
2g	Sn	Ph	Ph	H	20	-
2h	Sn	Ph	Ph_3Sn	H	30	30
2i	Sn	Ph	COOMe	H	80	20

mide is used with dimethylformamide as the solvent. The reaction is carried out in absolute ether by adding a solution of the benzhydroxamic acid chloride to a mixture of alkenylgermane and an equivalent amount of triethylamine. Initiation of the reaction is shown by the formation of a white precipitate of triethylammonium chloride.

In the case of the addition of pyridinehydroxamic acid chloride to alkenylgermanes, the reaction was carried out in dry benzene, mixing the acid chloride, the alkenylgermane and an equivalent amount of triethylamine.

Isoxazolines containing methyl, phenyl, *o*-difluoromethoxyphenyl, 2-, 3-, and 4-pyridyl groups at position 3 are viscous liquids or extremely low melting solids. With time in the presence of air they are oxidized and their colors change from light yellow to brown. In this connection the 3-isoxazoline substituted pyridines were converted to the more stable salts with hydrohalic acids. The [2+3]-dipolar cycloaddition of nitrile oxides to germyl substituted ethylene occurred regio- and stereospecifically to give 4-germyl substituted isoxazoline-2 derivatives, only one of the mixture of *E,Z* isomers reacts.

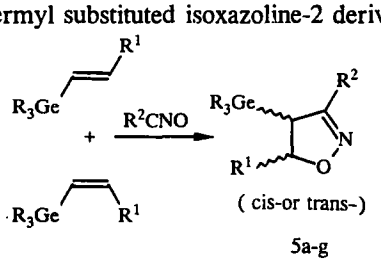
A mixture of isomers was formed in the cycloaddition to 1,2-disubstituted olefins [31, 32]. Electron donating amino [33] and alkoxy [34] substituents at the double bond lead to 5-substituted cycloadducts. Acyl [35, 36] and sulfinyl substituted [37] alkenes coordinate the oxygen of the nitrile oxide in position 4 of the cycloadduct.

The combined effects of alkoxy and acyl substituents gave high regioselectivity in the addition of nitrile oxides to 1,2-disubstituted alkenes [38]. The formation of small amounts of 4-substituted isoxazolines (4% in a mixture of regioisomers) was achieved in reactions of methyl and ethyl acrylates with nitrile oxides [39].

Addition of nitrile oxides to ethyl β-(E)-triethylsilylacrylate proceeded regioselectively to give E-4-triethylsilylsubstituted isoxazoline-2 [40].

Ethyl (E)-3-triethyl(phenyl)germylacrylate and ethyl β-triethyl(phenyl)germylstyrene were used as model compounds in a study of the regio- and stereochemistry of the cycloaddition of nitrile oxides to 1,2-disubstituted ethylenes.

β-(E,Z)-Germanyl substituted ethylenes react with nitrile oxides, generated by dehydration of nitroethane (nitropropane) in the presence of phenyl isocyanate and a catalytic amount of triethylamine in benzene (the Mukaiyama–Hoshito method [41]), to give the corresponding *cis*- and *trans*-4-germyl substituted isoxazoline-2 derivatives (Table 5).



5a-g

TABLE 3. Addition of Azides to Ethynylgermanes and Stannanes

Compound	M	R^1	R^2	R^3	Reaction time, h	Temperature, °C	Yield, %
3a	Ge	Me	CHO	H	24	20	81
3b	Ge	Et	CHO	H	60	20	74
3c	Ge	Me	CHO	4-$MeOC_6H_4$	20	110	46
3d	Ge	Me	CHO	4-$O_2NC_6H_4$	30	110	42
3e	Ge	Et	CHO	Ph	20	110	46
3f	Ge	Et	CHO	4-$MeOC_6H_4$	18	110	49
3g	Ge	Et	CHO	4-$O_2NC_6H_4$	26	110	38
3h	Ge	Et	Et_2N	4-$O_2NC_6H_4$	24	60	18
3i	Ge	Et	MePhN	4-$O_2NC_6H_4$	120	60	71
3j	Ge	Et	Ph_2N	4-$O_2NC_6H_4$	120	60	53
3k	Ge	Ph	Et_2N	4-$O_2NC_6H_4$	24	20	73
3l	Ge	Ph	MePhN	4-$O_2NC_6H_4$	48	20	74
3m	Ge	Ph	Ph_2N	4-$O_2NC_6H_4$	96	60	47
3n	Sn	Me	Et_2N	4-$O_2NC_6H_4$	5	60	73
3o	Sn	Ph	Et_2N	4-$O_2NC_6H_4$	1	20	39
3p	Sn	Ph	MePhN	4-$O_2NC_6H_4$	24	20	55
3q	Sn	Ph	Ph_2N	4-$O_2NC_6H_4$	48	20	44
3r	Ge	Ph	Et_2N	4-$Me_2NC_6H_4$	24	20	75
3s	Ge	Ph	Et_2N	4-$MeOC_6H_4$	0.1	20	71
3t	Ge	Ph	Et_2N	4-MeC_6H_4	0.1	20	74
3u	Ge	Ph	Et_2N	Me	0.1	20	67
3v	Ge	Ph	MePhN	4-$Me_2NC_6H_4$	48	20	61
3w	Sn	Ph	Et_2N	4-$MeOC_6H_4$	0.1	20	47
3x	Sn	Ph	Et_2N	4-MeC_6H_4	0.1	20	48
3y	Sn	Ph	MePhN	4-$Me_2NC_6H_4$	24	20	75
3z	Sn	Ph	MePhN	4-$MeOC_6H_4$	24	20	83
3aa	Sn	Ph	MePhN	4-MeC_6H_4	48	20	76

TABLE 4. Data on the Germyl Substituted Isoxazolines Produced

Compound	R	m	Yield, %
4a*	Me	0	45
4b	Ph	0	73
4c	o-$CHF_2OC_6H_4$	0	71
4d	Me	0	68
4e	Ph	0	70
4f	2-Py·HCl	0	70
4g	3-Py·HCl	0	47
4h	4-Py·HCl	0	45
4i	Me	1	42
4j	Ph	1	63
4k	2-Py·HCl	1	43
4l	3-Py·HBr	1	45
4m	4-Py·HBr	1	44

*n = 2 for compounds 4d and 4e; n = 1 for the rest.

Compounds 5a-e are colorless oils which are slowly oxidized in the air. Compounds 5f and 5g are white crystalline substances which are stable to moisture and light. No products were formed from the reaction of nitrile oxides with β-triphenylgermylstyrene because of steric hindrance and strong deactivation of the double bond by the phenyl and triphenylgermyl groups. In ethyl germylacrylate, germyl and carboethoxy groups, which have opposite electronic effects, are attached to the double bond and consequently formation of a mixture of isomers might be expected. However, both electronic and steric effects play major roles in cycloaddition reactions. In this case only one product is formed because of the very bulky germyl group at position 3. The carboethoxy and phenyl groups have different electrophilicities. It is probable that this determines the stereospecificity of the cycloaddition of nitrile oxides. The substituents on the germanium play no part in this.

TABLE 5. Data on the Stereospecifity of the Addition of Nitrile Oxides to Germylethylenes

Compound	R	R^1	R^2	Isomer	Yield, %
5a	Et	Ph	Me	*cis*	57
5b	Et	Ph	Et	*cis*	48
5c	Et	Ph	Ph	*cis*	57
5d	Et	COOEt	Me	*trans*	78
5e	Et	COOEt	Et	*trans*	74
5f	Ph	COOEt	Me	*trans*	94
5g	Ph	COOEt	Et	*trans*	90

TABLE 6. Results of Cycloaddition of Nitrile Oxides to Stannylacetylenes

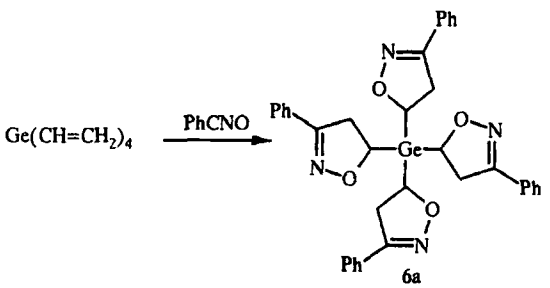
Compound	R	R^1	Yield, %
8a	Me	Me	73
8b	Me	Ph	93
8c	Me	COOEt	95
8d	Bu	Me	97
8e	Bu	Ph	100
8f	Bu	COOEt	85

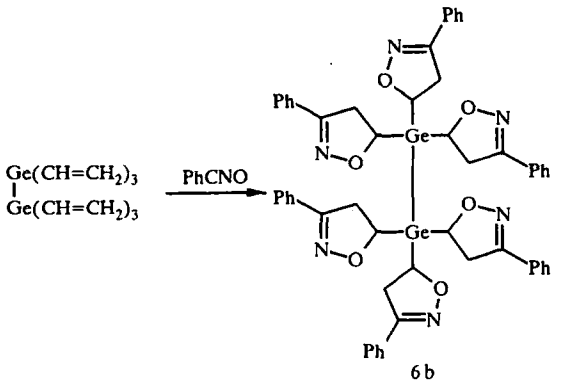
TABLE 7. Data on the Cycloaddition of Nitrile Oxides to β-Substituted Stannylacetylenes

Compound	R	R^1	Yield, %
9a	Bu	Me	48
9b	Bu	Ph	32
9c	Bu	COOEt	32
9d	Ph	Me	13
9e	Ph	Ph	15
9f	Ph	COOEt	88
9g	Me_3Si	Me	63
9h	Me_3Si	Ph	35
9i	Me_3Si	COOEt	95
9j	Me_3Sn	Me	67
9k	Me_3Sn	Ph	42
9l	Me_3Sn	COOEt	49

It can be noted that the yields of cycloaddition reactions are higher in the case of carboethoxy groups. Consequently, the higher the electronegativity, the greater the direction of polarization and the higher the yield of reaction products.

α-Germyl substituted ethylenes do not undergo [2+3]-cycloadditions with nitrile oxides because of steric hindrance. Nitrile oxides react actively with tetravinylgermane and hexavinyldigermane to give the corresponding tetra(3′-substituted-5-isoxazolinyl-2)germanes (45-47%) and hexa(3′-phenyl-5-isoxazolinyl)digermane (42%):

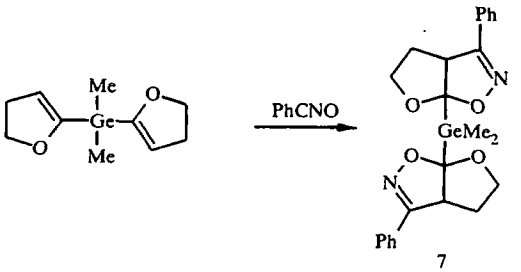




6b

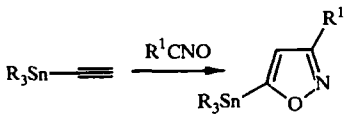
Addition of nitrile oxides to tetravinylgermane gave only one isomer, whereas in the case of hexavinyldigermane a mixture of diastereomers was formed as confirmed by ^1H NMR spectroscopy.

When benzonitrile oxide reacted with bis[5-(2,3-dihydrofuryl)]dimethyl germane in a 2:1 ratio a germane containing two condensed bicycles with four asymmetric centers was obtained in 68% yield. X-ray crystallography of bis[5-(3-methyl-3a,4,5,6a-tetrahydrofuro[2,3-*b*]isoxazolinyl)]germane confirmed that the molecule was chiral and existed in the form of SSRR/RRSS enantiomers. Benzonitrile oxide added stereospecifically to bis[5-(2,3-dihydrofuryl)]dimethylgermane, so that the hydrogen atoms in the molecule are in *cis*-position relative to the germanium atom. The distance between the germanium atom and the oxygen of the tetrahydrofurano and isoxazolinyl rings are 2.747(8) and 2.283(9) Å respectively. These values are less than the sums of the van der Waal's radii which might be interpreted as weak intramolecular interactions between the germanium and oxygen atoms. However, the geometry of the germanium atom remains tetrahedral [29].



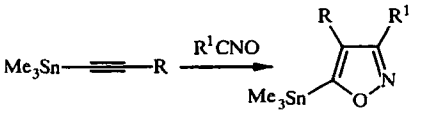
7

The reaction of trialklylstannylacetylene with nitrile oxides generated *in situ* in benzene occurs regiospecifically to give 3-substituted 5-trialkylstannylisoxazoles in excellent yields [42-47].



8a-f

β-Substituted stannylacetylenes react with nitrile oxides but in smaller yields [44-46]. The oxygen atom of the nitrile oxide adds regiospecifically to the carbon atom of the triple bond carrying the more electronegative substituent: C > Si > Sn.



9a-*l*

TABLE 8. Data on the Conversions of Stannylisoxazoles

Compound	R	Position of stannyl substituent	R^1	R^2	X	Reaction time, h	Yield, %
10a	Bu	3	H	—	NPh	72	54
10b	Bu	4	H	H	NPh	42	42
10c	Bu	5	—	H	NPh	20	0
10d	Bu	4	H	Me	O	3	85
10e	Bu	5	—	Me	O	3	80
11a	Bu	3	H	—	NPh	20	59
11b	Bu	4	H	H	NPh	24	49
11c	Bu	5	—	H	NPh	24	0
11d	Bu	4	H	Me	O	24	62(Ar=Ph)
11e	Bu	4	H	Me	O	36	74(Ar=3-Py)
11f	Bu	5	—	Me	O	7 (THF)	82(Ar=Ph)
11g	Bu	5	—	Me	O	6 (dioxane)	64(Ar=2-Py)
11h	Bu	5	—	Me	O	15 (dioxane)	60(Ar=3-Py)
12a	Bu	3	H	—	O	2	63
12b	Bu	3	COOEt	—	O	2	52
12c	Bu	3	H	—	NPh	1	94
12d	Bu	3, 4	H	—	NPh	0.3	68
12e	Bu	4	H	H	NPh	0.3	59
12f	Bu	5	—	H	NPh	0.3	61
12g	Me	5	—	Ph	O	2	48
12h	Me	5	—	COOEt	O	2	60
12i	Bu	4	—	Me	O	1	64
12j	Bu	5	—	Me	O	2	57

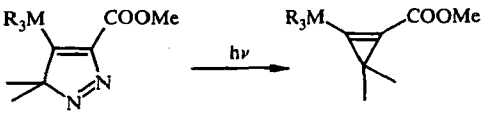
TABLE 9. Data on Desilylation (Destannylation)

Compound	M	R	R^1	R^2	Reaction time, h	Yield, %
13a	—	Me	—	Me	1.5	66
13b	—	Me	—	Ph	48	—
13c	—	Me	—	COOEt	6	49
13d	—	Bu	—	Me	24	70
14a	Si	—	Me	Me	2	60
14b	Si	—	Me	Ph	2	65
14c	Si	—	Me	COOEt	2	55

2. CHEMICAL PROPERTIES

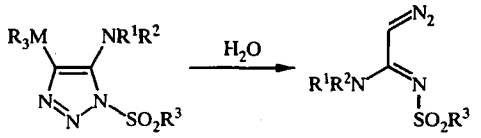
2.1. Conversions of Heterocycles and Carbofunctional Substituents

Elimination of a molecule of nitrogen to give quantitative formation of organometallic cyclopropenes occurred when dilute ether solutions of germyl- and stannylpyrazoles were irradiated with monochromatic light (λ = 190 nm) [5]:

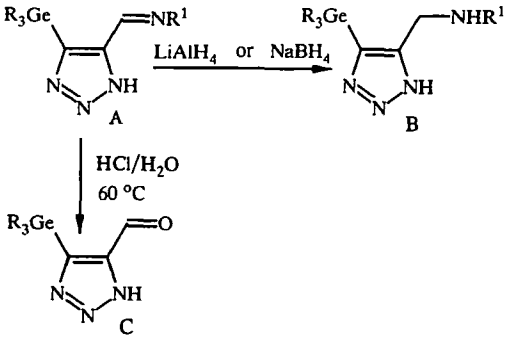


R = Alk , M = Ge, Sn

Ring opening of the triazole ring was noted when germyl- and stannyltriazoles were hydrolyzed with water [7]. Under these conditions, when the ring opened to give 2-diazoacetamidines in almost quantitative yield, scission of the M−C bond was also observed (M = Ge, Sn).

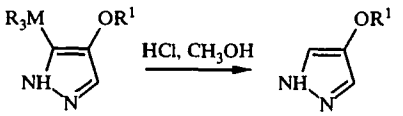


Germanium containing aldiminotriazoles A [16] were readily reduced with lithium tetrahydroaluminate in ether or sodium tetrahydroborate in methanol to the corresponding 4-trialkylgermyl-5-phenylaminomethyl-1,2,3-triazoles B. Reduction of silyltriazoles under analogous conditions was accompanied by desilylation. Splitting of the Ge−C bond on reduction with sodium tetrahydroborate was not observed even on boiling the reaction mixture. Degermylation of the aldimines was not achieved on heating to 100°C with potassium fluoride in dimethylformamide. Acid catalyzed hydrolysis also did not affect the germanium−carbon bond: 4-trialkylgermyl-1,2,3-triazol-5-carbaldehyde (C) was obtained on heating a methanol solution of the aldimine with 1 M hydrochloric acid at 60°C.

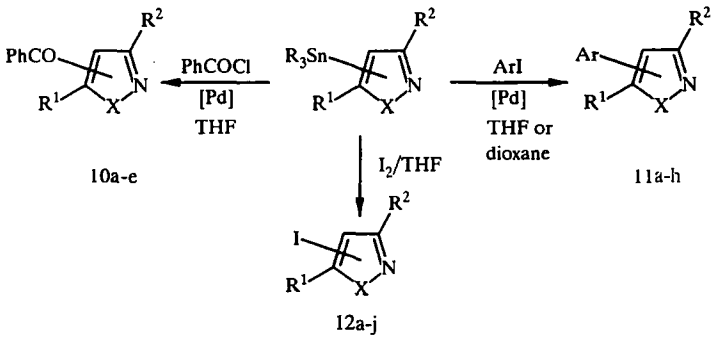


2.2. Demetallation Reactions

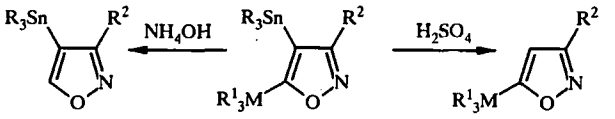
Hydrolysis of the germyl(stannyl) substituted alkoxypyrazoles 2a, b and f with hydrochloric acid on heating in methanol gave the alkoxypyrazoles in good yields (55-91%) by splitting of the metal−carbon bond [4].



Replacement of the stannyl group by iodine in stannylpyrazoles and stannylisoxazoles occurred relatively easily on treatment with iodine in tetrahydrofuran. Catalytic replacement of the stannyl substituent by benzoyl or aryl groups occurred in THF or dioxane in the presence of the palladium catalyst $[Pd(PPh_3)_2Cl_2]$ [42-46] (Table 8):

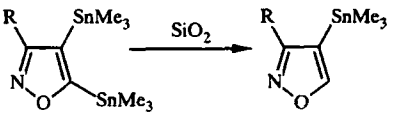


One of the metal groups is removed regiospecifically when 4,5-dimetal substituted isoxazoles reacted with sulfuric acid or aqueous ammonia to give a monometal substituted heterocycle (Table 9) [46, 47].



13a-d 14a-c

Reaction of 3,4-bis(trimethylstannyl)isoxazoles with silicon dioxide (contact with silica gel in polar solvents) caused quantitative elimination of the stannyl group at position 5 to give monostannyl substituted products 15 [47] where R = Alk or Ar.



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