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Addition of nitrile oxides to germyl-substituted ethylenes

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Abstract

The reactions of [2 + 3] cycloaddition of nitrile oxides to mono- and 1,2-disubstituted germylalkenes proceed regioselectively and resulted 5-Ge-substituted isoxazolines-2 from triethylvinyl- and triethylallylgermane and 4-Ge-isomers from β-triorganylgermylstyrene and ethyl triorganylgermylacrylates. In the latter case the reaction occurs stereospecifically: *Z*-germylalkenes give *cis*-, while *E*-germylalkenes yield *trans*-4,5-substituted isoxazolines. The structure of products obtained was determined by ^{1}H-NMR spectroscopy and for **11a** confirmed by single-crystal X-ray analysis.

Keywords: Germanium; Hydrogermylation; Cycloaddition; Isoxazolines-2; X-ray structure

1. Introduction

Alkenyl- and alkynyl germanes have been involved in various [2 + 3] cycloaddition reactions. The addition of diazoalkanes to unsaturated germanes resulting in germyl-substituted pyrazoles and pyrazolines has been described [1,2]. Germylacetylenes add organic azides to give 1,2,3-triazoles [3]. The interaction of inorganic azides with germanium containing α,β-acetylenic aldehydes and aldimines [4] has been studied as well. In all cases the mixture of regioisomers has been obtained.

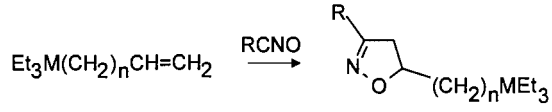
However, up to now the reaction of nitrile oxides with alkenylgermanes has not been studied.

The direction of cycloaddition of nitrile oxides to alkenylsilanes depends on the type of a substituent at the double bond [5]. To find out the regularities of this reaction in the series of alkenylgermanes we have studied the addition of nitrile oxides to triethylvinyl and triethylallylgermane, β-triorganylgemylstyrenes and ethyl triorganylgermylacrylates.

2. Results and discussion

2.1. Interaction of nitrile oxides with triethylvinylgermane and triethylallylgermane

It has been found that triethylvinylgermane and triethylallylgermane readily react with nitrile oxides in the cycloaddition reaction affording regiospecifically the corresponding 5-germyl-substituted isoxazolines-2 with good yields (42–73%).



The reactions with triethylvinylsilane proceed analogously.

Nitrile oxides were obtained using two methods of generation: (1) from the primary nitroalkanes in the presence of phenylisocyanate and the catalytic amount of triethylamine; (2) from hydroxamic acid chlorides in the presence of bases as acceptors of hydrogen chloride.

Following the first method the reaction was carried out in benzene dropping nitroethane with the catalytic amount of triethylamine to the mixture of alkenylger-

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mane, double equivalent of phenylisocyanate and 1 ml triethylamine. Release of CO_2 and precipitation of diphenylurea evidenced for the beginning of the reaction. The addition of nitrile oxide to germylalkene is considered as a terminal stage of the reaction. Therefore, it is extremely important to drop nitroethane slowly to avoid the formation of furoxan.

The second method appears to be convenient as well, but there is still one drawback in this method—chlorination of aldoximes. During the chlorination of benzaldoximes the side reaction, chlorination of the ring, often occurs. To avoid any side reactions *N*-chlorosuccinimide was used for chlorination in dimethylformamide. The addition reaction was carried out in ether dropping the solutions of benzhydroxamic acid chloride to the mixture of alkenylgermane and the equivalent amount of triethylamine. The precipitation of triethylamine hydrochloride marks the beginning of the reaction.

According to GLC and mass-spectroscopic data only one product is obtained in the reactions of cycloaddition (Table 1). ^{1}H-NMR data evidence that 5-triethylsilyl(germyl)-substituted isoxazoline is formed. The signals of two protons (H_a and H_b) in 4 position of isoxazoline appear in the spectrum of compound **1**: H_a at δ 2.53 ppm: (ddq, $^4J = 0.65$ Hz, coupling with protons of the methyl group in 3 position, $^2J = 13.3$ Hz–coupling with H_b, $^3J = 15.91$ Hz, coupling with H_c) and H_b at δ 2.97 ppm: (ddq, $^4J = 0.65$ Hz, $^3J = 10.9$ Hz, $^3J = 15.91$ Hz). H_c in 5 position resonates in lower field as one of the substituents is an oxygen atom δ: 3.95 ppm: (dd, $^3J = 10.9$ Hz, coupling with H_b, $^3J = 15.91$ Hz–with H_a).

^{1}H-NMR data for compound **3** are similar: H_a at δ 2.8 ppm: (ddq, $^4J = 0.2$ Hz, coupling with protons of the methyl group in 3 position, $^3J = 14.2$ Hz, coupling with H_b, $^3J = 14.2$ Hz, coupling with H_c); H_b at δ 3.09 ppm: (ddq, $^4J = 0.2$ Hz, coupling with protons of the methyl group in 3 position, $^2J = 10$ Hz, coupling with H_b, $^3J = 14.2$ Hz, coupling with H_c). Proton H_c in 5 position resonates at δ 4.16 ppm: (dd, $^3J = 10$ Hz, coupling with H_c, $^3J = 14.2$ Hz, with proton H_a).

^{1}H-NMR data for compound **5** differ to some extent due to the methylene group in 5 position. Signals of the methylene protons (H_d, H_e) appear in the higher fields: H_d at δ 1.30 ppm: (dd, $^2J = 6.1$ Hz, coupling with H_d, $^3J = 13.3$ Hz, coupling with H_a) and H_e at 1.32 ppm: (dd, $^2J = 6.1$ Hz, coupling with H_e, $^3J = 13.3$ Hz, coupling with H_a). Signals of protons H_a and H_b are assigned analogously to H_a and H_b in compounds **1** and **3**: H_a at δ 2.46 ppm: (ddq, $J = 1.09$, 9.15 and 16.57 Hz), H_b at 2.94 ppm: (ddq, $J = 1.09$, 9.6 and 16.57 Hz). The signal of H_c proton is shifted down field and appears at δ 4.96 ppm (m).

Table 1
5-Ge(Si)-substituted isoxazolines-2

Number	R	*n*	M	Yield (%)
1	Me	0	Si	54
2	Ph	0	Si	76
3	Me	0	Ge	45
4	Ph	0	Ge	73
5	Me	1	Ge	42
6	Ph	1	Ge	63

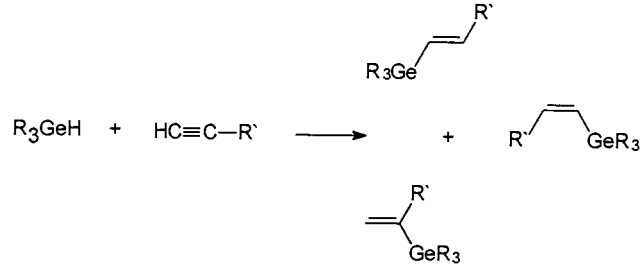
Polarization of the vinyl group in triethylvinylgermane and triethylallylgermane is opposite and, consequently, one can expect the different regioselectivity of nitrile oxides addition, while it has been proved experimentally that the addition occurs analogously. Addition of benzonitrile oxide to 3,3-dimethylbutene proceeds in the same direction affording 3-phenyl-5-*t*-butylisoxazoline-2 [5]. Trimethylvinyl- and trimethylallylsilane in [2 + 3]-cycloaddition reactions with nitrile oxides also give only one product 5-Si-substituted isoxazoline-2 [5].

The addition to terminal alkenylsilanes proceeds regiospecifically: the oxygen atom always attacks the more substituted carbon atom. The relative reactivity of the alkenylsilanes in cycloaddition of benzonitrile oxide decreases at the insertion of the methylene groups between silicon and the double bond [6].

2.2. Hydrogermylation of acetylenes with trisubstituted germanes

To obtain β-germyl-substituted ethylenes necessary for the investigation of cycloaddition reaction the hydrogermylation of the substituted acetylenes with triorganylgermanes has been used.

Triethyl(phenyl)germane adds to the substituted acetylenes in the presence of Speier's catalyst (0.1 M solution $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol). The reaction with triethylgermane was carried out without solvent, while diethyl ether was used as a solvent in the hydrogermylation with triphenylgermane. The reactions of triethylgermane with phenylacetylene and ethyl propiolate were exothermic, but to initiate the hydrogermylation with triphenylgermane some heating was needed.



R = Et, Ph.
R`= Ph, COOEt.

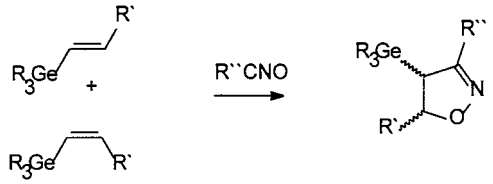
Table 2
Isomers ratio in the hydrogermylation reaction (GLC data)

Number	R	R′	*Z* (%)	*E* (%)	α (%)
7a	Et	COOEt	14	34	52
7b	Et	Ph	10	58	32
8a	Ph	COOEt	10	31	59
8b	Ph	Ph	9	43	48

α- And β-isomers were formed approximately in equal amounts, while β-(*E*)-isomer was formed predominantly if compared with β-(*Z*)-isomer (Table 2).

2.3. Interaction of nitrile oxides with β-(E,Z)-germylsubstituted ethylenes

β-(*E*,*Z*)-Germyl-substituted ethylenes react with nitrile oxides, generated by the dehydration of nitroethane (nitropropane) with phenylisocyanate in the presence of the catalytic amount of triethylamine in benzene (Mukaiyama's method) [7], and benzonitrile oxide, generated by the dehydrohalogenation of benzhydroxamic acid chloride with triethylamine in ether, affording *cis*- or *trans*-4-germyl-substituted isoxazolines-2 (Table 3):



Compounds **9a**, **9b**, **10a** and **10b** are viscous liquids. They are gradually oxidized under storage. Their color changes from colorless to light orange. Compounds **11a**, **11b** are white crystalline substances stable to moisture and light.

According to GLC and mass-spectroscopic data only one product is resulted from [2 + 3]-cycloaddition reactions. Nitrile oxide reacted with only one of the isomers. After the separation of the reaction mixture in each case the product and the unreacted second isomer were obtained.

Table 3
4-Ge-substituted isoxazolines-2

Number	R	R′	R″	Isomer	Yield(%)
9a	Et	Ph	Me	*cis*	57
9b	Et	Ph	Et	*cis*	48
9c	Et	Ph	Ph	*cis*	57
10a	Et	COOEt	Me	*trans*	78
10b	Et	COOEt	Et	*trans*	74
11a	Ph	COOEt	Me	*trans*	94
11b	Ph	COOEt	Et	*trans*	90

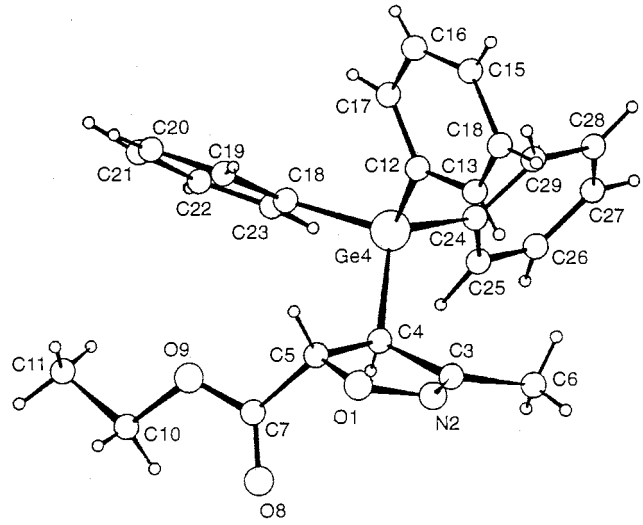


Fig. 1. Molecular structure of ethyl ester of 3-methyI-4-triphenygermyI-5-isoxazoline-2-carboxylic acid

According to ^{1}H-NMR spectroscopic data 4-triethyl(phenyl)germyl- substituted isoxazolines are formed. For compound **9a** the signal of proton H_a in position 4 appears at δ 2.73 ppm (dd, $^4J = 1.8$ Hz, coupling with protons of the methyl group in 3 position, $^3J = 5$ Hz, coupling with H_b). The signal at δ 5.44 ppm (d, $J = 5$ Hz) was assigned to the proton H_b in 5 position of isoxazoline, as 5-carbon is linked with an oxygen atom and phenyl group.

The structure of 4-germyl-substituted isoxazoline-2 for compound **11a** is confirmed by X-ray diffraction analysis. A perspective view of the molecule **11a** with the atom labels is shown in Fig. 1. The izoxazoline ring of **11a** has the envelope conformation. The dihedral angle between O1, N2, C3, C4 plane and the triangle O1, C5, C4 is equal 171.5(4)°. Atom C5 deviates from O1, N2, C3, C4 plane by 0.131(6) Å; the displacement of C6 from the plane is 0.022(10) Å. The triphenylgermyl and ethoxycarbonyl substituents in regard to C4–C5 bond are partially eclipsed: the torsion angle Ge1–C4–C5–C7 is 123.4(5)°, the molecule has + anti-clynal form in accordance with Klyne and Prelog nomenclature [8]. Table 5 lists the bond lengths and the values of valence angles for molecule **11a**.

According to ^{1}H-NMR only *Z*-isomer of, β-triethyl(phenyl)germylstyrene reacted with nitrile oxides affording *cis*-cycloadduct. It is confirmed by the spin–spin coupling constants of H_a and H_b protons: $^3J = 5.0$ Hz for compounds **9a** and **9b** and $^3J = 3.2$ Hz for compound **9c**. The cycloaddition of nitrile oxides to ethyl β-triethyl(phenyl)germylacrylate occurred only with *E*-isomer giving *trans*-product; the spin–spin coupling constants $^3J = 16$ Hz (**10a**), 14.8 Hz (**10b**), 13.3 Hz (**11a**), 12.86 Hz (**11b**) support this fact.

α-Ge-substituted ethylenes under the same reaction conditions did not react with nitrile oxides obviously

due to the steric hindrance at the α-carbon atom of the double bond.

A mixture of regioisomers is usually obtained in [2 + 3] cycloaddition reactions of nitrile oxides with 1,2-disubstituted alkenes [9,10], although electron-donating amino [11] and alkoxy [12] substitutents tend to orientate the cycloaddition so that they are at 5 position in the cycloadducts. Acyl [13,14] and sulfinyl [15] substituents direct the oxygen of the nitrile oxide so that they are at 4 position of the cycloadduct [16]. The combined effects of the alkoxy and acyl substitutents resulted in the high regioselectivity of nitrile oxides addition to β-(*E*)-methoxyvinylphenylketone [17]. 4-isomer appears also in the case of interaction of acrylates and nitrile oxides, the reaction results in 4% of 4-isomer and 96% of 5-isomer [18].

The oxygen of nitrile oxides attacks β-carbon atom of the double bond, e.g. in *N*-substituted indoles [19], uracils [20], β-(*E*)-methoxyvinylphenylketone [17] and 2-ethyl-2-crotyl-1,3-dithiane-1-oxide [16].

Table 4
Atomic coordinates and equivalent isotropic temperature factors* (with e.s.d.'s) for **11a**

Atom	*x*	*y*	*z*	B_{eq}
Ge1	0.24179(4)	0.08588(5)	0.38986(3)	0.0361 (2)
O1	−0.0707(4)	−0.0623(4)	0.3068(3)	0.0795(14)
N2	−0.0389(4)	−0.0502(5)	0.2456(3)	0.0608(14)
C3	0.0389(5)	0.0411(6)	0.2565(3)	0.0460(13)
C4	0.0734(4)	0.1063(5)	0.3275(3)	0.0390(12)
C5	−0.0135(5)	0.0397(6)	0.3569(3)	0.0497(14)
C6	0.0877(8)	0.0774(11)	0.2003(4)	0.074(2)
C7	−0.1031(5)	0.1357(7)	0.3644(3)	0.061(2)
O8	−0.1930(4)	0.1637(7)	0.3184(3)	0.116(2)
O9	−0.0691(4)	0.1872(5)	0.4283(2)	0.0726(13)
C10	−0.1412(7)	0.2936(9)	0.4424(4)	0.082(2)
C11	−0.0804(11)	0.3313(13)	0.5192(5)	0.101 (3)
C12	0.2845(5)	−0.1005(5)	0.4061(3)	0.0425(12)
C13	0.2476(6)	−0.1952(6)	0.3513(3)	0.060(2)
C14	0.2867(7)	−0.3256(6)	0.3623(4)	0.071(2)
C15	0.3672(7)	−0.3615(8)	0.4265(4)	0 070(2)
C16	0.4060(6)	−0.2726(7)	0.4808(4)	0.069(2)
C17	0.3647(5)	−0.1422(6)	0.4705(3)	0.055(2)
C18	0.2575(4)	0.1739(6)	0.4798(3)	0.0428(13)
C19	0.2379(6)	0.1099(7)	0.5349(3)	0.061 (2)
C20	0.2549(7)	0.1731(9)	0.5986(3)	0.076(2)
C21	0.2922(6)	0.3009(9)	0.6093(4)	0.074(2)
C22	0.3082(8)	0.3691(8)	0.5540(4)	0.082(2)
C23	0.2904(7)	0.3059(7)	0.4896(4)	0.067(2)
C24	0.3451(4)	0.1694(5)	0.3466(2)	0.0390(12)
C25	0.3279(5)	0.2998(6)	0.3210(3)	0.0451(13)
C26	0.4079(6)	0.3622(7)	0.2954(3)	0.062(2)
C27	0.5051(6)	0.2929(8)	0.2946(4)	0.072(2)
C28	0.5242(6)	0.1623(8)	0.3187(3)	0.063(2)
C29	0.4452(5)	0.1025(6)	0.3446(3)	0.0471(14)

B_{eq} (Å^2) calculated from anisotropic thermal parameters as $B_{eq} = 8\pi^2 D_u^{1/3}$ where D_u is a determinant of the U_{ij} matrix in orthogonal space.

The addition of nitrile oxide to ethyl β-*trans*-triethylsilylacrylate proceeds regiospecifically to give *trans*-4-triethylsilyl-substituted isoxazoline-2 [4].

It may be concluded that during the reactions of [2 + 3] cycloaddition of nitrile oxides to 1,2-disubstituted ethylenes the oxygen attacks the most electropositive carbon atom of the double bond.

In the reactions with β-triethylgermylstyrene and ethyl β-triethylgermylacrylate the oxygen of nitrile oxide also attacks the carbon atom bearing phenyl- or ethoxycarbonyl substituents affording 4-Ge-substituted isoxazolines-2.

3. Experimental

^{1}H-NMR spectra were recorded on a Bruker WH-90/DS (90 MHz) and an AM360/DS (360.1 MHz) instruments at 303 K with TMS as internal standard. Mass spectra were recorded on a Kratos MS-25 apparatus (70 eV). GLC analysis was perfomed on a Varian 3700 instrument equipped with flame-ionizing detector using a capilar column 5 m × 0.53 mm, df = 2.65 μ, HP-1. Carrier gas-nitrogen.

The melting points were determined on a 'Digital melting point analyzer' (Fisher), the results are given without correction.

3.1. X-Ray structure determination of compound **11a**

Monocrystals of compound **11a** were grown from petroleum ether. The crystals (0.25 × 0.30 × 0.50mm) were measured on a Syntex $P2_1$, four-circle computer controlled single-crystal difractometer with graphite-monochromated Mo–K_α (λ = 0.71069 Å) radiation; lattice parameters were refined from 18 reflections with $30 < 2\theta < 35°$. A total of 4028 unique reflection intensities were collected at room temperature using the $\theta/2\theta$ scan technique up to $2\theta_{max} = 50°$ (sin $\theta/\lambda = 0.595$ Å^{-1}); one standard reflection showed no significant decay; Lorentz and polarization corrections were applied to the data.

Crystallographic data for **11a** are: monoclinic; a = 12.080(2), b = 10.011(2), c = 20.072(3) Å, β = 110.52(1)°; V = 2273.3(6) Å^3, Z = 4, μ = 1.37 mm^{-1}, D_{calc} = 1.344(1) g cm^{-3}; F(000) = 952; space group $P2_1$/c. For crystal structure solution, the initial phases of ten strong reflections were determined by the maximum determinant method [21]. The phase values obtained were introduced into the starting set of the MULTAN program [22]. Two variants were calculated, one of them yielding the structure model. The structure was refined by least squares technique in the full matrix approximation with anisotropic temperature factors. The hydrogen atoms were found from different synthesis and refined isotropically. The final goodness of fit

Table 5
Bond lengths (Å) and angles (°) with e.s.d.'s for molecule **11a** (H atoms not involved)

Ge1–C12	1.933(5)	C12–C13	1.400(8)
Ge1–C24	1.942(5)	C13–C14	1.380(8)
Ge1–C18	1.957(5)	C14–C15	1.362(10)
Ge1–C4	1.990(5)	C15–C16	1.358(10)
O1–N2	1.415(6)	C16–C17	1.387(8)
O1–C5	1.430(7)	C18–C19	1.369(7)
N2–C3	1.273(7)	C18–C23	1.374(8)
C3–C4	1.488(7)	C19–C20	1.376(9)
C3–C6	1.490(9)	C20–C21	1.349(10)
C4–C5	1.526(7)	C21–C22	1.372(10)
C5–C7	1.494(9)	C22–C23	1.387(9)
C7–08	1.186(7)	C24–C25	1.391(7)
C7–O9	1.308(7)	C24–C29	1.395(7)
O9–C10	1.464(8)	C25–C26	1.392(8)
C10–C11	1.506(12)	C26–C27	1.368(9)
C12–C17	1.381(7)	C27–C28	1.386(10)
		C28–C29	1.373(8)
C12–Ge1–C24	108.4(2)	C17–C12–Ge1	120.5(4)
C12–Ge1–C18	110.2(2)	C13–C12–Ge1	121.9(4)
C24–Ge1–C18	110.4(2)	C14–C13–C12	121.2(6)
C12–Ge1–C4	111.0(2)	C15–C14–C13	119.4(7)
C24–Ge1–C4	110.5(2)	C16–C15–C14	121.2(7)
C18–Ge1–C4	106.3(2)	C15–C16–C17	119.5(6)
N2–O1–C5	109.8(4)	C16–C17–C12	121.5(6)
C3–N2–O1	108.7(4)	C19–C18–C23	117.2(5)
N2–C3–C4	115.0(5)	C19–C18–Ge1	123.1(4)
N2–C3–C6	120.5(6)	C23–C18–Ge1	119.7(4)
C4–C3–C6	124.4(6)	C18–C19–C20	121.6(7)
C3–C4–C5	100.3(4)	C21–C20–C19	121.1(7)
C3–C4–Ge1	116.0(4)	C20–C21–C22	118.5(7)
C5–C4–Ge1	113.7(4)	C21–C22–C23	120.5(7)
O1–C5–C7	110.0(5)	C18–C23–C22	121.0(6)
O1–C5–C4	105.5(4)	C25–C24–C29	117.3(5)
C7–C5–C4	112.3(5)	C25–C24–Ge1	122.2(4)
O8–C7–O9	123.9(6)	C29–C24–Ge1	120.4(4)
O8–C7–C5	124.7(6)	C24–C25–C26	121.6(6)
O9–C7–C5	111.3(5)	C27–C26–C25	119.1(6)
C7–O9–C10	118.2(5)	C26–C27–C28	120.8(6)
O9–C10–C11	1105.6(7)	C29–C28–C27	119.4(6)
C17–C12–C13	117.1(5)	C28–C29–C24	121.7(6)

and *R*-factor are 0.953 and 0.0565, respectively. The program SHELXL-93 [23] were used for calculations. The final coordinates and thermal parameters for non-hydrogen atoms are listed in Table 4.

3.2. General methods of preparation

3.2.1. Method A

Nitroethane (0.02 mol) and triethylamine (two drops) in dry benzene (40 ml) were added dropwise during 4 h to the mixture of germyl(silyl)substituted ethylene (0.02 mol), phenylisocyanate (0.04 mol) and triethylamine (1 ml) in dry benzene at room temperature. After some minutes CO_2 begins to release and diphenylurea precipitates. The mixture is heated for 4 h at 70–80°C. After cooling to room temperature diphenylurea is filtered, the solvent removed using the rotating evaporator.

3.2.2. 3-Methyl-5-triethylsilylisoxazoline-2 (**1**), b.p. = 102°C/3mm

^{1}H-NMR (360.1 MHz,$CDCl_3$/TMS) δ (ppm): 0.65 (6H, q, $J = 8.06$ Hz); 0.99 (9H, t, $J = 8.06$ Hz); 2.02 (3H, dd, $J = 0.66$ Hz, $J = 1.09$ Hz); 2.53 (1H, ddq, $J = 0.65$, 13.3, 15.91 Hz); 2.97 (1H, ddq, $J = 0.65$, 10.9, 15.91 Hz); 3.95 (1H, dd, $J = 10.9$, 15.91 Hz).

GC MS(70 eV, m/z): 199 [M^+], 197, 185, 169, 157, 128(100), 114(12), 100(60), 86(39), 58(20), 43(13), 39(8).

3.2.3. 3-Methyl-5-triethylgermylisoxazoline-2 (**3**), b.p. = 68°C/1mm

^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ (ppm): 0.71 (15H, m); 2.04 (3H, t, $J = 0.2$ Hz); 2.80 (1H, ddq, $J = 0.2$, 10, 14.2 Hz); 3.09 (1H, ddq, $J = 0.2$, 10, 14.2 Hz); 4.16 (1H, dd, $J = 10$, 14.2 Hz).

GC MS(70 eV, m/z): 218, 217, 216 [M^+-29], 215, 214, 213, 212, 175(22), 173(16), 171 (12), 161 (29), 160(15), 159(23), 157(17), 135(20), 133(100), 132(28), 131 (79), 129(57), 117(10), 107(16), 105(80), 104(20), 103(81), 101(67), 99(19), 91(13), 89(15), 87(12), 77(15), 75(26), 74(15), 73(22), 71(11), 56(10), 42(10), 41(56).

3.2.4. 3-Methyl-5-triethylgermylmethylisoxazoline-2 (**5**), b.p. = 92°C/1mm

^{1}H-NMR (360.1 MHz,$CDCl_3$/TMS) δ (ppm): 0.78 (6H, q, $J = 7.68$ Hz); 1.03 (9H, t, $J = 7.68$ Hz); 1.10 (1H, dd, $J = 6.1$, 13.3 Hz); 1.32 (1H, dd, $J = 6.1$, 13.3 Hz); 1.97 (3H, t, $J = 1.09$ Hz); 2.46 (1H, ddq, $J = 1.09$, 9.15, 16.57 Hz); 2.94 (1H, ddq, $J = 1.09$, 9.6, 16.57 Hz); 4.96(1H, m).

GC MS(70 eV, m/z): 258 [M^+], 256, 254, 230(30), 229(14), 228(25), 227(20), 149(37), 147(30), 145(22), 133(8), 131(15), 130(12), 128(10), 105(17), 103(22), 102(18), 99(8), 91(11), 89(10), 87(7), 82(17), 75(9), 73(11), 71 (8), 60(12), 43(16), 42(46), 41(100), 39(38), 30(32).

3.2.5. 3-Methyl-4-triethylgermyl-5-phenylisoxazoline-2 (**9a**)

The pure product was isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ (ppm): 0.72–1.28 (15H, m), 1.96(3H, t, $J = 1.8$ Hz), 2.73(1H, dd, $J = 1.8$, 5 Hz), 5.44(1H, d, $J = 5$ Hz), 7.20–7.31(5H, m).

GC MS(70 eV, m/z):321([M^+]), 320, 319, 318, 292(19), 291, 290, 288, 278, 278, 277, 276, 266, 265, 264, 263, 262, 237, 236, 235(20), 234(16), 233(17), 161(28), 160(11), 159(18), 133(83), 132(66), 131(58), 105(80), 103(82), 101(47), 91(28), 77(57), 44(100). 3-Ethyl-4-triethylgermyl-5-phenylisoxazoline-2 (**9b**).

The pure product was isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ (ppm): 0.84–01.26 (18H, m), 2.31 (2H, q, $J = 8$ Hz), 2.78 (1H, d, $J = 5$ Hz), 5.44 (1H, d, $J = 5$ Hz), 7.26–7.34 (5H, m).

GC MS (70 eV, m/z): 355 (18[M^+]), 354 (16), 353(11), 307, 306(20), 305(17), 303(11), 235(20), 234(18), 232(12), 160(37), 159(35), 158(49), 135(18), 133(92), 131(82), 130(63), 105(96), 103(100), 101(52), 91(39), 77(61).

3.2.6. (3-Methyl-4-triethylgermylisoxazolinyl-2)-5-carboxylic acid ethyl ester (**10a**)

The pure product was isolated by column chromatography on silica gel with 5:1 hexane:ethyl acetate as eluent.

^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ (ppm): 0.89–1.15 (15H, m), 1.31 (3H, t, $J = 6.9$ Hz), 2.0 (3H, d, $J = 1.2$ Hz), 3.04 (1H, dd, $J = 1.2$, 15.1 Hz), 4.27 (2H, q, $J = 6.9$ Hz), 4.57 (1H, d, $J = 15.1$ Hz).

GC MS(70 eV, m/z):288([M-29]), 287, 284, 281, 262, 260, 259, 258, 255, 248(10), 247(45), 246(31), 243(22), 163, 161(41), 160(37), 159(21), 134(22), 133(100), 132(78), 130(58), 104(54), 103(58), 101(46), 90(14), 89(15), 77(11), 75(18), 74(9), 70(16), 44(83), 29(22).

3.2.7. (3-Ethyl-4-triethylgermyl-isoxazolinyl-2)-5-carboxylic acid ethyl ester (**10b**)

The pure product was isolated by column chromatography on silica gel with 5:1 hexane:ethyl acetate as eluent.

^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ (ppm): 0.91–1.12 (18H, m), 1.14(3H, t, $J = 7.6$ Hz), 2.21 (2H, q, $J = 7.1$ Hz), 3.08 (1H, dd, $J = 1$, 14.8 Hz), 4.25 (2H, q, $J = 7.6$ Hz), 4.51 (1H, d, $J = 14.8$ Hz).

GC MS(70 eV, m/z): 302 [M-29], 301, 298, 262(10), 261(18), 260(15), 243(10), 175(52), 174(41), 173(20),133(100), 132(70), 130(41), 105(78), 103(51), 101 (41), 90(14), 89(15), 68(81), 29(28).

3.2.8. (3-Methyl-4-triphenylgermyl-isoxazolinyl-2)-5-carboxylic acid ethyl ester (**11a**)

^{1}H-NMR (360.1 MHz,$CDCl_3$/TMS) δ (ppm): 1.11(3H, t, $J = 7.2$ Hz), 1.92 (3H,d, $J = 1.08$ Hz), 3.95–4.04 (2H, m), 4.08 (1H, dq, $J = 1.08$, 2.04, 11.99 Hz), 5.27 (1H, d, $J = 13.3$ Hz), 7.37–7.42 (9H, m), 7.54–7.57 (6H, m). M.p. = 116°C (from petroleum ether). Anal. found: C, 65.18; H, 5.48; N, 3.00. $C_{25}H_{25}GeNO_3$ calc.: C, 65.27; H, 5.48; N, 3.04%.

3.2.9. (3-Ethyl-4-triphenylgermyl-isoxazolinyl-2)-5-carboxylic acid ethyl ester (**11b**)

^{1}H-NMR (360.1 MHz,$CDCl_3$/TMS) δ (ppm): 1.03 (3H, t, $J = 7.41$ Hz), 1.12 (3H, t, $J = 7.19$ Hz), 2.17 (1H, dq, $J = 1.08$, 7.19 Hz), 2.38 (1H, dq, $J = 0.89$, 7.41 Hz), 4.01 (2H, qua, $J = 7.19$ Hz), 4.12 (1H, dt, $J = 1.08$, 12.86 Hz), 5.28 (1H, d, $J = 12.86$ Hz), 7.37–7.44 (10H, m), 7.54–7.56 (6H, m). M.p. = 114°C (from petroleum ether/pentane (10:1)). Anal. found: C, 65.91; H, 5.79; N, 2.88. $C_{26}H_{27}GeNO_3$ calc.: C, 65.87; H, 5.74; N, 2.95%.

3.3. Method B

Benzhydroxamic acid chloride (0.02 mol) in dry ether (20 ml) was added dropwise for 2 h to the mixture of germylsubstituted ethylene (0.02 mol) and triethylamine (0.02 mol) in dry ether (30 ml) at room temperature. After some minutes triethylamine hydrochloride precipitated. The mixture was refluxed for 2 h. Triethylamine hydrochloride was filtered off, the solvent removed using the rotating evaporator.

3.3.1. 3-Phenyl-5-triethylsilylisoxazoline-2 (**2**)

The pure product was isolated by column chromotography on silica gel with 5:1 hexane:ethyl acetate as eluent.

^{1}H-NMR (360.1 MHz,$CDCl_3$/TMS) δ (ppm): 0.6 (6H, dq, $J = 2.83$, 7.41 Hz), 0.92 (9H, t, $J = 7.41$ Hz), 3.03 (1H, dd, $J = 15.7$, 15.92 Hz), 3.34 (1H, dd, $J = 11.34$, 15.7 Hz), 4.05 (1H, dd, $J = 11.34$, 15.92 Hz), 7.27-7.29 (3H, m), 7.58–7.61 (2H, m).

3.3.2. 3-Phenyl-5-triethylgermylisoxazoline-2 (**4**), m.p. = 7–10°C (from petroleum ether)

^{1}H-NMR (360.1 MHz, $CDCl_3$/TMS) δ (ppm): 0.951 (15H, m); 3.16 (1H, dd, $J = 15.25$, 15.84 Hz); 3.51 (1H, dd, $J = 10.86$, 15.25 Hz); 4.37 (1H, dd, $J = 10.86$, 15.84 Hz); 7.31–7.79 (5H, m).

3.3.3. 3-Phenyl-5-triethylgermylmethylisoxazoline-2 (**6**), m.p. = 20–22°C (from petroleum ether)

^{1}H-NMR (360.1 MHz, $CDCl_3$/TMS) δ (ppm): 0.84 (6H, q, $J = 8.29$ Hz); 1.06 (9H, t, $J = 8.29$ Hz); 1.20 (1H, dd, $J = 6.54$, 13.3 Hz); 1.40 (1H, dd, $J = 6.54$, 13.3 Hz); 2.88 (1H, dd, $J = 9.15$, 16.35 Hz); 3.38 (1H, dd, $J = 9.81$, 16.35 Hz); 4.90 (1H, m); 7.40 (3H, m); 7.65 (2H, m).

3.3.4. 4-Triethylgermyl-3,5-diphenylisoxazoline-2 (**9c**)

The pure product was isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ (ppm): 0.76–1.15 (15H, m), 3.93 (1H, d, $J = 3.2$ Hz), 5.73 (1H, d, $J = 3.2$ Hz), 7.28–7.41 (5H, m), 7.51–7.73 (5H, m).

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