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Si-, Ge- and Sn-diine derivatives in 1,3-dipolar cycloaddition reactions

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Abstract

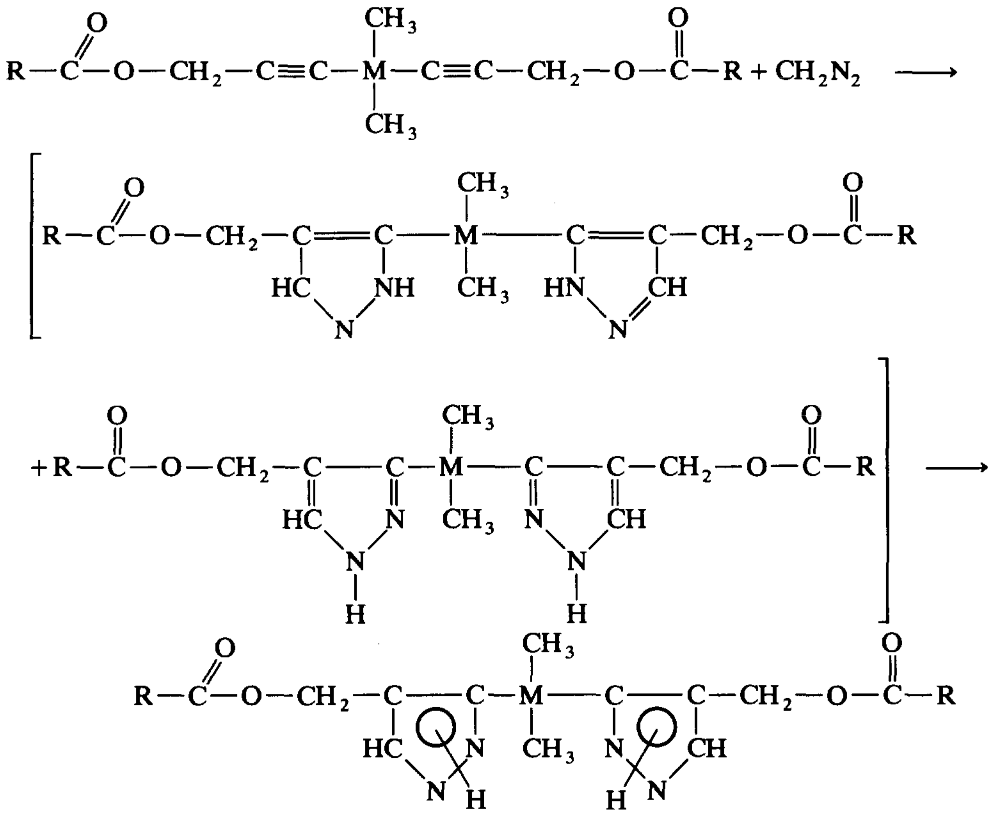
1,3-Dipolar diazomethane cycloaddition to element-substituted diine ethers where M = Si, Ge, Sn results in formation of 3,3′(5,5′)-dimethylelement-4,4′-benzoyloxymethylpyrazoles.

The present work is devoted to investigation of the 1,3-dipolar cycloaddition reaction between element-substituted (Si,Ge,Sn)-benzoyloxyacetylenes and diazomethane.

It is established that the nucleophilic carbon atom in diazomethane is added regioselectively to the carbon atom of the triple bond that is in the β-position to the element–organic residue, forming 3,3′(5,5′)-dimethylelement-4,4′-benzoyloxymethylpyrazoles according to Scheme 1, where M = Si (a), Ge (b), Sn (c); R = Ph (Ia,b,c); 2-Cl-C_6H_4 (IIa,b,c); 4-Cl-C_6H_4 (IIIa,b,c); 2,4-Cl_2-C_6H_4 (IVa,b,c).

The course of the reaction was followed by monitoring the disappearance of an IR-spectrum absorption band in the region of 2168–2200 cm^{-1}, which corresponds to valency fluctuations in the carbon–carbon triple bond, and the appearance of a new band in the area of 3200–3260 cm^{-1} that is characteristic for fluctuations in valency of the NH group of the pyrazole formed.

In the ^1H NMR spectrum of pyrazole the proton at the carbon atom in the 3,3′(5,5′) position forms a singlet in the area of 7.3–7.7 ppm. According to the data available [1] protons of a pyrazole ring in the 3(5) position have chemical shifts of 7.4–7.6 ppm. The protons of the $-OCH_2$ group appear in the region of 5.4–5.6 ppm, and those of an aromatic ring, in the area of 7.9–8.2 ppm.



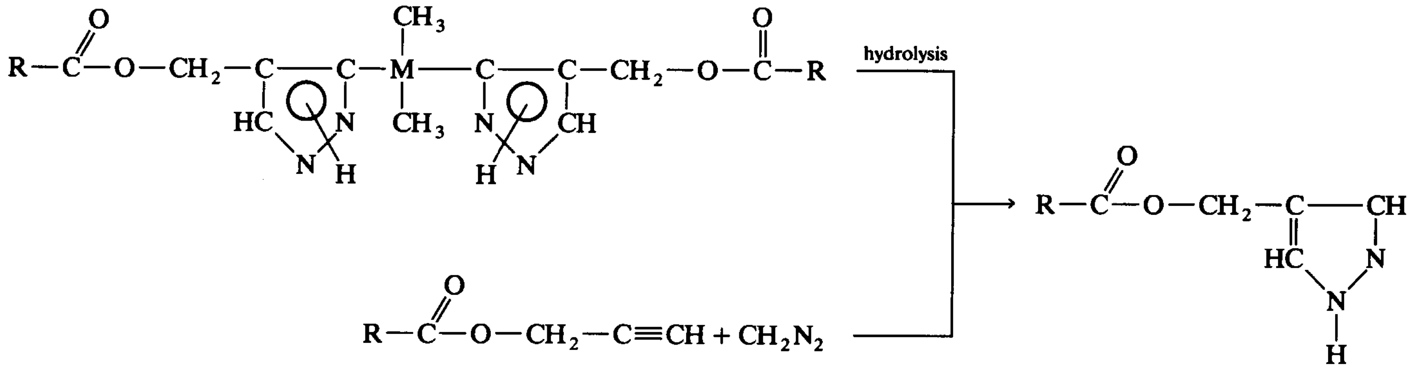
Scheme 1.

To confirm that the addition of diazomethane to element-substituted diine ethers proceeds in the above direction the products were hydrolysed with hydrochloric acid in methanol, resulting in element–carbon bond rupture and formation of 4-benzoyloxymethylpyrazole (II) (Scheme 2).

In the ^1H NMR-spectra of the hydrolysis products protons of the group $-OCH_2$ appear in the region of 5.3–5.4 ppm, protons of an aromatic ring in the region of 67.6–8.0 ppm and protons of the NH group in the region 6.65–7.9 ppm. 4-Benzoyloxymethylpyrazoles without an element–organic group were synthesized by cycloaddition of diazomethane via a triple bond of the propargylic ether of benzoic acid derivatives [2]. Constants and spectral characteristics of benzoyloxymethylpyrazoles obtained by these two methods were found to be identical.

It should be noted here that in the ^1H NMR spectra of element-substituted pyrazoles signals are shifted into a weaker field as compared with 4-benzoyloxymethylpyrazoles. The lowering of the chemical shift of the proton of the NH group is especially great. Such a shift can be explained by postulating greater involvement of a nitrogen electron pair of this group into conjugation with the ring, made possible by introduction of an electron-accepting substituent prompting redistribution of electron density of the ring.

Thus, 1,3-dipolar diazomethane cycloaddition to element-substituted diine ethers results in formation of 3,3′(5,5′)-dimethylelement-4,4′-benzoyloxymethylpyrasoles (I–IV(a,b,c).



Scheme 2.

Experimental

IR-spectra were recorded on a Specord-75 spectrophotometer (with KBr).

^{1}H NMR-spectra were recorded in a Varian spectrometer, 100 mHz with DMSO as an internal standard (the values are given according to the δ scale).

Diazomethane was obtained from nitrosomethylurea [3].

Reaction of diazomethane with 3,3′-bis-(propyne-1,1-benzoate)-dimethylsilane (Ia)

1.0 g of 3,3′-bis-(propyne-1,1′-benzoate)-dimethylsilane was placed in a conical flask and 0.929 (0.02 g · mol) of fresh diazomethane solution was gradually added to 25 ml of diethyl ether. The reaction mixture was kept in darkness at 0 ° C. As decolorization of the yellow solution was observed fresh portions of diazomethane were added to maintain the yellow colour. The solvent was then evaporated and the product purified by the FLC method over Al_2O_3 in the system benzene : hexene (4 : 10). $R_f = 0.59$. The fusion point is 180–181° C. All pyrazoles I(b,c)–IV(a,b,c) were obtained under similar conditions.

Hydrolysis of 3,3′(5,5′)-dimethylsilanil-[4,4′-bis-(benzoyloxymethyl-]-bis-pyrazole (Ia)

1.5 g of Ia was mixed with 40 g of methanol and 3 ml of concentrated HCl. The mixture was boiled in a flask with a condenser stirring for 12 days and nights. Then 20 g of KOH were added and a multiple extraction with ether was performed. Ether extracts were dried over $MgSO_4$ and 0.8 g of 4-benzoyloxymethylpyrazole was obtained. The fusion point is 59–60 ° C [2]. All the other element-substituted pyrazole-derivatives were subjected to hydrolysis under similar conditions.

References

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