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METHOD FOR OBTAINING SILYL(GERMYL)-SUBSTITUTED *o*-DIFLUOROMETHOXYPHENYLISOXAZOLINES

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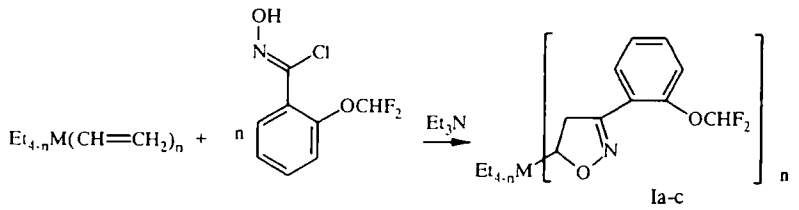
It was shown earlier [1] that reactions of [2+3]-cycloaddition of nitrile oxides to unsaturated silanes lead to formation of silyl-substituted 2-isoxazolines. With the goal of obtaining new potentially biologically active heterocycles containing a germyl substituent and a difluoromethoxyphenyl group, we developed a preparative method for synthesis of germyl-substituted *o*-difluoromethoxyphenyl-2-isoxazolines by cycloaddition of *o*-difluoromethoxybenzonitrile oxide to triethylvinylsilane (germane) and diethyldivinylgermane.



I a M = Si, n = 1; b M = Ge, n = 1; c M = Ge, n = 2

Nitrile oxide was obtained *in situ* by dehydrohalogenation of *o*-difluoromethoxybenzoxamic acid chloride in the presence of an equivalent amount of triethylamine. The reaction proceeds regioselectively with formation of 5-Ge-substituted 2-isoxazolines in good yields (67-80%). Unfortunately, the compounds Ia-c obtained are colorless oils, and become tarry on contact with air and moisture and also on standing, changing color from light yellow to red-brown. So their future use as biologically active substances is extremely limited.

3-(*o*-Difluoromethoxyphenyl)-5-triethylsilyl-2-isoxazoline (Ia). A solution of 0.02 moles *o*-difluoromethoxybenzoxamic acid chloride in 20 ml dry ether was slowly added with rapid stirring to a mixture of an equivalent amount of triethylvinylsilane and triethylamine in 30 ml ether at room temperature for 2 h. Almost immediately after the reaction began, a precipitate of triethylamine hydrochloride fell out of solution. The precipitate was filtered off, the solution was evaporated, the residue was chromatographed on silica gel (eluent, hexane–ethyl acetate, 5:1). Yield, 80%. Mass spectrum (*m/z*, relative intensity, %): 327 (M^+, 7), 150 (35), 129 (100), 101 (75), 87 (51), 59 (56). PMR spectrum ($CDCl_3$): 0.73 (6H, d, J = 8.1 Hz); 1.04 (9H, t, J = 8.1 Hz); 3.27 (1H, dd, J = 10.6, J = 17.2 Hz); 3.57 (1H, dd, J = 10.6, J= 17.2 Hz); 4.2 (1H, dd, J = 10.6, J = 17.2 Hz); 6.61 (1H, s); 7.41 (1H, m); 7.49 (1H, d, J = 2 Hz); 7.84 (1H, d, J = 2 Hz); 7.92 (1H, d, J = 2 Hz).

3-(*o*-Difluoromethoxyphenyl)-5-triethylgermyl-2-isoxazoline (Ib). Mass spectrum (*m/z*, relative intensity, %): 373 (M^+), 330 (18), 161 (100), 133 (45), 101 (37). Yield, 72%. PMR spectrum ($CDCl_3$): 0.82-1.25 (15H, m); 3.21 (1H, dd, J = 15.6, J = 15.6 Hz); 3.63 (1H, dd, J = 10.2, J = 15.6 Hz); 4.44 (1H, dd, J = 10.2, J = 15.6 Hz); 6.58 (1H, s); 7.19 (3H, m); 7.82-7.94 (1H, m).

Bis-5-(3-*o*-difluoromethoxyphenyl-2-isoxazolino)diethylgermane (Ic). Yield, 67%. PMR spectrum ($CDCl_3$): 1.02-1.25 (10H, m); 3.36-3.64 (4H, m); 4.52 (2H, dd, J = 10.1, J = 15.2 Hz); 6.52 (2H, s); 7.09-7.41 (6H, m); 7.64-7.80 (2H, m).

REFERENCES

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