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VINYL MONOMERS CONTAINING 1,2-THIA-, -SELENA- AND -TELLURAZOLE SYSTEMS, THEIR POLYMERS AND COPOLYMERS

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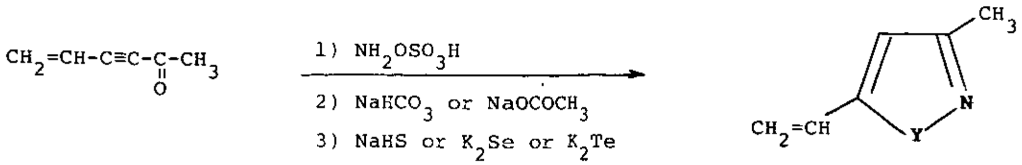
Abstract - 3-Methyl-5-vinyl-1,2-tellurazole, -selenazole, and -thiazole have been prepared by one pot reaction from 5-hexen-3-yn-2-one, hydroxylamine-O-sulphonic acid and the proper alkaline chalcogenide. Their radical homopolymerization and copolymerization with styrene have been investigated.

Recently some of us described the first method for the synthesis of 1,2-tellurazole derivatives[1] which resulted of general validity in the preparation of 4-unsubstituted derivatives and was extended for the obtainment of the isologues 1,2-selenazoles[2] and 1,2-thiazoles.[3] Further researches in this field now enable us to prepare vinyl derivatives of the three above-mentioned heterocyclic systems useful as precursors of polyfunctional polymers containing either the unaltered heterocycles or various 1,3-difunctional groups after transformation of the rings under different reaction conditions.[4,5]

We here report the synthesis of the first 5-vinyl-substituted 1,2-chalcogenazoles together with a concise study about their polymerization behaviour.

According to our findings the profitable 5-hexen-3-yn-2-one (**1**) is transformed into 3-methyl-5-vinyl-1,2-chalcogenazoles (**2**) through one pot procedure by treating it with hydroxylamine-O-sulphonic acid, then with the proper alkaline chalcogenide in buffered aqueous solution (Scheme 1).



1

2

a: Y = S
b: Y = Se
c: Y = Te

Scheme 1

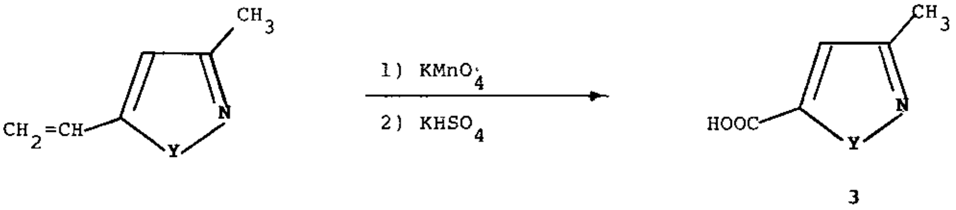
The reaction yields decrease going from sulphur to selenium to tellurium parallel with the reductive power increase of the chalcogenide and probably with the aromatic character decrease of the corresponding heterocycle. The 3-methyl-5-vinyl-1,2-tellurazole (**2c**) is prepared in poor yields, nevertheless it is the first example of a vinyl monomer of an heteroaromatic system with N-Te bonds.

A possible reaction mechanism involves the initial transformation of the carbonyl group into an oxime-O-sulphonic acid which can be monitored by the disappearance of the ketone odor, then the addition of the chalcogenide in buffered solution may imply a nucleophilic attack of the chalcogenide ion to the triple bond according to known reactions[6] and the subsequent cyclization by nucleophilic displacement of the sulphate anion. It is relevant to note that the oxime-O-sulphonic acids and their analogues react with reducing agents to give imines or carbonyl compounds after hydrolysis.[7]

The preparation of the ketone **1** has been carefully examined referring to the known procedure of Petrov.[8] Vinylacetylene, prepared according to Backer,[9] is treated with ethylmagnesium bromide as by Petrov, while the subsequent addition of 1,2-dibromoethyl ethyl ether, dehydrohalogenation with potassium hydroxide and decomposition of the enol ether with sulphuric acid are substituted by the simple addition of the vinylacetylenic Grignard reagent at -70 °C to an ethereal solution of acetic anhydride. The pure ketone **1** is obtained after hydrolysis.

Structures **2a-c** are in agreement with elemental analysis and IR and NMR spectroscopic data which are resumed in Table 1. In the NMR spectra the monotone shifting towards higher fields of the proton of CH_2 which is trans to vinyl CH clearly evidences the increasing shielding effect in the series sulphur, selenium, tellurium and confirms that the preferred conformation of the vinyl group is that with the CH_2 group oriented towards the chalcogen atom, as it has been proved in the case of other vinyl derivatives like 2-vinylfuran and 2-vinylthiophene.[10]

Molecular structures of vinyl derivatives **2 a,b** have also been confirmed by their conversion after reaction with neutral $KMnO_4$ into the known carboxylic acids **3a,b**[11,12] according to Scheme 2.



3

a: Y = S

b: Y = Se

Scheme 2

As far as the obtained monomers are concerned, both **2a** and **2b** are oils which may be purified by distillation at reduced pressure, while **2c** is a solid which may be sublimated or crystallized. All of them easily polymerize in solution with radical initiators.

Table 1. Characteristic data of 3-methyl-5-vinyl-1,2-chalcogenazoles

Compound	bp °C/torr	IR cm^{-1}	^1H-NMR ($CDCl_3$)
2a	64-66/18	1522,1345,809, 568(ring), 1623,978,915(vinyl)	2.46(3H, s, methyl), 5.42(1H,d,H_{cis} of CH_2, J=10.9 Hz), 5.73(1H,d,H_{trans} of CH_2, J=17.5 Hz), 6.80(1H, s, ring proton), 6.90(1H, dd, vinyl CH)
2b	87-90/18	1538,1329,748, 428(ring), 1622,990,937(vinyl)	2.43(3H, s, methyl), 5.46(1H,d,H_{cis} of CH_2, J=10.6 Hz), 5.59(1H,d,H_{trans} of CH_2, J=17.3 Hz), 6.86(1H, dd, vinyl CH), 7.06(1H, s, ring proton)
2c	48-50[a]	1550,1320,728, 383(ring), 1620,975,905(vinyl)	2.45(3H, s, methyl), 5.40(1H,d,H_{trans} of CH_2, J=16.7 Hz), 5.48(1H,d,H_{cis} of CH_2, J=10.2 Hz), 6.87(1H, dd, vinyl CH), 7.72(1H, s, ring proton)

[a] melting point °C after crystallization from ether

Monomers **2a** and **2b**, more profitable than **2c** from a practical point of view owing to their higher preparation yields, have been submitted to a more extensive study. Both **2a** and **2b** in dioxane solution at 60 °C with 3% w/w azobisisobutyronitrile (AIBN) as initiator well polymerize and copolymerize in various ratios with styrene (STY), the usual reference comonomer, in agreement with a strong activation effect of the heterocycles. The fractionated homopolymers and copolymers are well preservable white powders. Tables 2 and 3 summarize preparation conditions and properties of some homopolymers and copolymers.

IR spectra of homopolymers and copolymers as well as nitrogen elemental analysis of homopolymers confirm the presence of unaltered heterocyclic rings. IR spectra and nitrogen elemental analysis on further fractionated copolymers account for real copolymers rather than for polymer mixtures.

Table 2. Homopolymers and Copolymers of **2a** and **2b**

Monomer	Comonomer	Molar ratio	Dioxane ml/mol of monomers	Weight conversion %	Time min	Solvents	Non solvents
2a	-	1	282	53.4	476	a,b,c,e,h	d,f,g
2a	STY	1:0.99	150	44.7	495	a,b,c,e,h	d,f,g
2b	-	1	295	43.4	587	a,b,c,e,h	d,f,g
2b	STY	1:1.04	228	35.2	505	a,b,c,e,h	d,f,g

a=benzene; b=chloroform; c=dichloromethane; d=diethyl ether; e=dioxane; f=methanol; g=petrol ether 40-60 °C; h=tetrahydrofuran

Table 3. Composition data, osmometric number average molecular weight and IR band values of the homopolymers and copolymers of **2a** and **2b** reported in Table 2

Polymer	M_1[a]	% N in the polymer	m_1[b]	$\overline{Mn}$	$\nu(cm^{-1})$
2a	1.00	11.20[c]	1.00	15000[d]	1533, 1359, 816, 580
2a/STY	0.50	7.76	0.65	14000[e]	1528, 1348, 810, 574
2b	1.00	7.98[f]	1.00	5700[d]	1547, 1334, 728, 429
2b/STY	0.49	6.73	0.74	7000[d]	1547, 1334, 728, 429

[a] M_1 = mol fraction of the heterocyclic monomer in the feed

[b] m_1 = mol fraction of the heterocyclic monomer in the copolymer

[c] % N calculated for C_6H_7NS = 11.18

[d] in dichloromethane at 26 °C

[e] in benzene at 37 °C

[f] % N calculated for C_6H_7NSe = 8.14

EXPERIMENTAL

Melting points were determined with a Reichert Thermovar apparatus and are uncorrected. IR spectra were recorded as KBr pellets or films on a Perkin Elmer 1330 spectrophotometer. ^{1}H-NMR spectra were measured in $CDCl_3$ with TMS as internal standard on a Bruker 300 spectrometer. Molecular weights were determined on a Knauer Vapour Pressure Osmometer. Microanalyses of the 1,2-chalcogenazole monomers were in satisfactory agreement with the calculated values (C$\pm$0.20, H$\pm$0.12, N$\pm$0.23).

5-Hexen-3-yn-2-one (**1**). A solution of 47.64 g (466.6 mmol) of rectified acetic anhydride in 100 ml of anhydrous ether was treated under nitrogen and stirred at -70 °C with 142 ml of a 2.37M ether solution of 3-buten-1-ynylmagnesium bromide[8] for 40 min. The mixture after stirring for 1 h at -70 °C and 30 min at room temperature was hydrolyzed with 100 ml of water at 0 °C, then it was extracted with 100 ml of ether in three portions. The extracts were concentrated, stirred for three hours with an equal volume of water and extracted again with 100 ml of ether in three portions. The extracts were washed with saturated $NaHCO_3$ and dried over anhydrous sodium sulfate. After removal of the solvent the residue was fractionated at reduced pressure affording 8.67 g (92.1 mmol) of 1. bp 58-59 °C/28 torr (lit.[8] 38-39 °C/10 torr).

3-Methyl-5-vinyl-1,2-thiazole (**2a**). The ketone 1 (10.08 g; 107.1 mmol) was treated with 40 ml of distilled water at 0 °C then with 12.44 g (110.0 mmol) of hydroxylamine-O-sulphonic acid and vigorously stirred at the same temperature for 25 min up to the disappearance of the ketone odor, then it was added with 8.92 g (106.2 mmol) of $NaHCO_3$ and treated with 60.4 ml of 1.94M aqueous solution of NaSH. The mixture was stirred for 4 h at room temperature, then steam distilled. The distillate was extracted with ether and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled at reduced pressure to afford 2.95 g (23.6 mmol) of **2a**. Yield 22%.

3-Methyl-5-vinyl-1,2-selenazole (**2b**). The compound 1 (10.51 g; 111.7 mmol) was treated with 100 ml of deoxygenated water at 0 °C then with 12.63 g (111.7 mmol) of hydroxylamine-O-sulphonic acid and stirred under nitrogen at the same temperature for 25 min up to the disappearance of the ketone odor. The mixture was added with 30.41 g (223.5 mmol) of sodium acetate trihydrate and treated during 40 min with 186 ml of 0.6M aqueous solution of potassium selenide.[13a] The mixture, stirred for 4 h at room temperature, extracted with 400 ml of ether in five portions and dried over anhydrous sodium sulfate was distilled at reduced pressure to afford 3.85 g (22.4 mmol) of **2b**. Yield 20 %.

3-Methyl-5-vinyl-1,2-tellurazole (**2c**). The compound 1 (9.10 g; 96.7 mmol) was treated with 100 ml of deoxygenated water at 0 °C, then with 10.94 g (96.7 mmol) of hydroxylamine-O-sulphonic acid and stirred under nitrogen at the same temperature for 25 min up to the disappearance of the ketone odor. The mixture was added with 26.32 g (193.4 mmol) of sodium acetate trihydrate and treated during 40 min with 161 ml of 0.6M aqueous solution of potassium telluride.[13b] The mixture was stirred for 4 h at room temperature and then extracted with 400 ml of ethyl acetate in five portions. The extracts were washed with water, dried over anhydrous sodium sulfate and distilled at reduced pressure up to the removal of the solvent. The residue was added with 100 ml of ether and extracted with 90 ml of 0.5M HCl in three portions. The acid aqueous solution was filtered, treated with concentrated aqueous ammonia up to pH=10 and extracted with 200 ml of dichloromethane in five portions. The extracts after drying over sodium sulfate and removal of the solvent at reduced pressure afforded 1.06 g (4.80 mmol) of **2c** (yield 5 %) which was purified by sublimation at 0.01 torr and crystallization from ether at -30 °C.

Reaction of **2a** *with* $KMnO_4$.The compound **2a** (0.102 g; 0.81 mmol) suspended in 5 ml of water was treated dropwise with a 0.1M aqueous solution of $KMnO_4$ at room temperature up to persistent colour. After filtration, the solution was acidified up to pH 1 with $KHSO_4$ and extracted with 50 ml of ether in three portions. The extracts after drying over anhydrous sodium sulfate were evaporated to afford 0.041 g (0.29 mmol) of a solid compound having melting point and IR spectrum coincident to that of authentic 3-methylisothiazole-5-carboxylic acid (**3a**).[11]

Reaction of **2b** *with* $KMnO_4$. The compound **2b** (0.086 g; 0.50 mmol) was oxidized with $KMnO_4$ as above described affording 0.031 g (0.16 mmol) of a solid whose IR spectrum was superimposable to that of an authentic sample of 3-methylisoselenazole-5-carboxylic acid (**3b**).[12]

Homopolymerizations and copolymerizations. Polymerization experiments were carried out by stirring at 60 °C a mixture of monomers and solvent in desired ratios together with AIBN 3% w/w introduced under nitrogen in a receiver with screw cap, silicone rubber septum and stirring bar. Polymers and copolymers obtained by low conversion reaction were precipitated by pouring the reaction mixture into petrol ether 40-60 °C. Crude polymer samples were purified by two dissolution/precipitation cycles in dichloromethane/petrol ether 40-60 °C and dried under vacuum at 30 °C for 24 h.

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