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VINYL DERIVATIVES OF HETEROCYCLIC SYSTEMS AND THEIR POLYMERS: 3-VINYL-1,2,5-THIADIAZOLE

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Abstract—3-Vinyl-1,2,5-thiadiazole is prepared by different methods: by one-pot reaction from 1,2,5-thiadiazole, by cyclization of 3,4-diamino-1-butene, and by the Wittig procedure either from 1,2,5-thiadiazolylmethylenetriphenylphosphorane or from 3-formyl-1,2,5-thiadiazole. Some physical and chemical properties are described.

Some stable heterocycles may be transformed by suitable reagents into functionalized acyclic systems; therefore they may be considered to be masked forms of such groups. Assuming that this could be exploited in the preparation of polyfunctionalized polymers, we focussed our attention on 3-vinyl-1,2,5-thiadiazole **1** as starting material for the synthesis of macromolecules containing 1,2-diamino, -diimino, or -dicarbonyl groups.

This paper deals with the synthesis of **1** which was carried out first by conventional preparations, then by one-pot procedure starting from the unsubstituted 1,2,5-thiadiazole. We found that 1,2,5-thiadiazole gives compound **1** by reaction with vinylmagnesium chloride, then with sulphur dichloride (Scheme 1).

Under the conditions examined, the method affords only 15% yields; nevertheless, apart from its theoretical interest, it is a simple procedure and it makes use of easily accessible reagents. Yields varied with other sulphurating agents in place of sulphur dichloride, reaching 18% with 1-piperidinesulphenyl chloride,[1] and 10% with sulphur monochloride, while they dropped to zero with tetrasulphur tetranitride, or with 1,1'-thiodiimidazole.[2]

The mechanism of the reaction probably involves as first step a nucleophilic attack at the sulphur atom and cleavage of the ring in analogy to what is known for disubstituted 1,2,5-thiadiazoles.[3] The chemistry of the process appears to be rather complex, and therefore any further discussion on this matter is necessarily postponed until further data on the behaviour of other substrates and reagents are available for comparison. A further point of interest in the reaction of Scheme 1 is that other Grignard reagents give analogous results affording, sometimes in good yields, other 1,2,5-thiadiazoles.

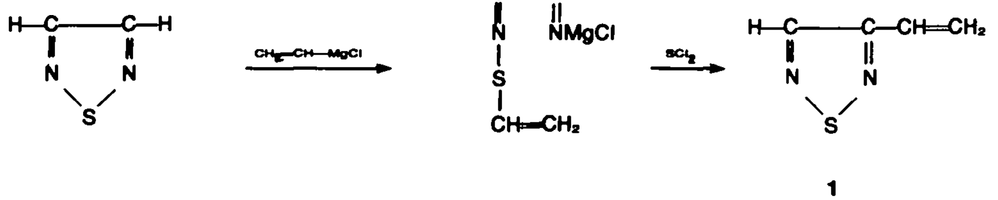
The other preparations of **1** started respectively from 3,4-diamino-1-butene[4] **2**, or, by Wittig reaction, either from 1,2,5-thiadiazolylmethylenetriphenylphosphorane[5,6] **3** or from 3-formyl-1,2,5-thiadiazole[5,7] **4** according to the reactions of Scheme 2 (see Experimental section).

The cyclization of 3,4-diamino-1-butene with N,N'-ditosylsulphur diimide, in double stoichiometric amount to avoid the formation of the dihydrothiadiazole derivative,[8] gives rather good yields, but the preparative value of this reaction is limited by the tedious preparation of the diamine. Other traditional cyclizing agents like sulphur chlorides in place of N,N'-ditosylsulphur diimide were discarded owing to their high reactivity towards double bonds.

The laborious preparation of reagents represents a disadvantage also for syntheses starting from **3** or **4**. Moreover **4** is unstable while **3** if not under very dry conditions gives some 3-methyl-1,2,5-thiadiazole, which causes a very difficult purification of the compound **1**.

The molecular structure of **1** is clearly proved by elemental analysis and IR and NMR spectra. Moreover compound **1** is easily oxidized to 1,2,5-thiadiazole-3-carboxylic acid by potassium permanganate, and brominated with bromine to the racemic 3-(1,2-dibromoethyl)-1,2,5-thiadiazole **5**.

Compound **1** forms a stable complex with metal ions. With an aqueous solution of cadmium chloride, **1** yields a



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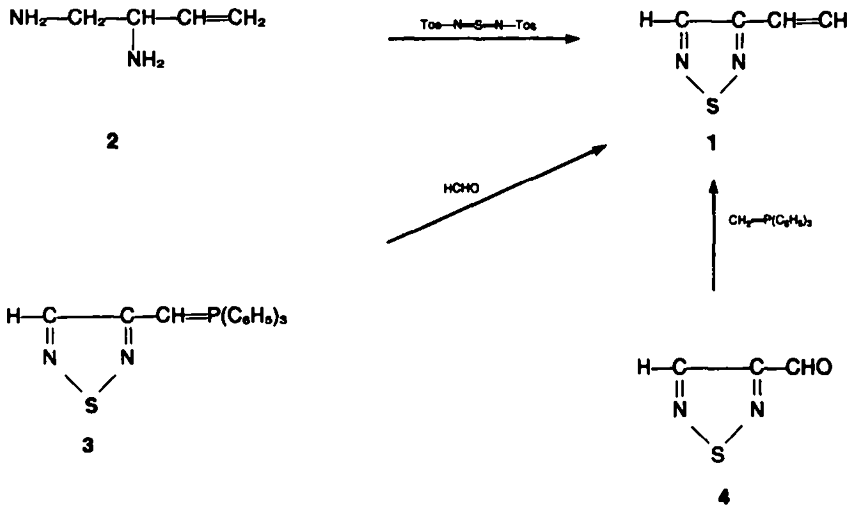
Scheme 1.



Scheme 2.

white crystalline precipitate which is indefinitely stable in a closed vessel and easily releases the thiadiazole product by distillation of its aqueous suspension.

Compound 1 easily polymerizes and copolymerizes with radical initiators yielding macromolecules containing 1,2,5-thiadiazole rings.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 225 spectrophotometer. UV spectra were determined with a Cary 14 spectrophotometer. NMR spectra were run on a Jeol PS 100 instrument (Me_4Si as internal standard).

3-*Vinyl*-1,2,5-*thiadiazole* 1

Method(a). A THF solution (65 ml) of 0.18 mol of vinylmagnesium chloride under N_2 was added to 120 ml of anhydrous ether, cooled to −50°, and treated dropwise under stirring in about 2 h with a solution of 5.00 g (58.06 mmol) of 1,2,5-thiadiazole in 65 ml of anhydrous ether. The mixture was stirred at unchanged temperature for 2.5 h, then it was treated dropwise during 2 h with 9.26 g (89.93 mmol) of purified SCl_2 (b.p. 59°) in 80 ml of anhydrous ether. After the addition the cold bath was removed and the stirring continued for 3 h. The mixture was treated with 400 ml of water, acidified with few drops of hydrochloric acid and subjected to a rapid steam distillation. The distillate, about 200 ml, was saturated with ammonium sulphate, extracted with peroxides-free ether, and dried over anhydrous sodium sulphate. After removal of the solvent the residue was added with potassium hydroxide pellets and distilled under nitrogen at reduced pressure. Compound 1 (0.972 g, 8.67 mmol) was collected at 50–51°/19 Torr and purified further by eluting the product from a 25 mm diameter column of 70 g of Florisil (30–60 mesh; B.D.H.) with n-pentane–ether (90:10), and subsequent distillation. $n_D^{25} = 1.5435$; λ_{max} (iso-octane) 218 nm (ϵ 7100, fine structure), 276 nm (ϵ 10800), 281 nm (ϵ 10600); ν_{max} (film) 1630, 1417, 986, 931 (vinyl), 831, 788, 610, 511 cm^{-1} (ring); δ (neat; Me_4Si ext. ref.) 8.38 (1H, s, ring proton), 6.62 (1H, q, vinyl CH), 5.80 (1H, q, H_{trans} of the CH_2 group), 5.26 (1H, q, H_{cis} of the CH_2 group). Found: C, 42.96; H, 3.67; N, 24.79; S, 28.73. $C_4H_4N_2S$ requires: C, 42.84; H, 3.59; N, 24.98; S, 28.59%.

Method(b). A mixture of 6.891 g (18.60 mmol) of N,N′-ditosylsulphur diimide,[9] 80 ml of anhydrous carbon tetrachloride and 0.660 g (7.66 mmol) of 3,4-diamino-1-butene was stirred 24 h at room temp., then it was filtered. The filtrate was washed with few milliliters of water, dried over anhydrous sodium sulphate, distilled up to the removal of the solvent, added with few pellets of potassium hydroxide and distilled as reported under method(a). Yield of 1 was 0.192 g (1.71 mmol).

Method(c). A 58.95 mmol sample of gaseous formaldehyde, prepared by heating 1.77 g of paraformaldehyde, was carried by N_2 through a solution of 21.12 g (58.60 mmol) of well purified 1,2,5-thiadiazolylmethylenetriphenylphosphorane 3 in 150 ml of anhydrous methylene chloride, maintained at 0° under stirring. The bubbling decolourized the solution up to cream yellow. The ice bath was removed and the solution was stirred for 15 min. The reaction mixture, quenched with 25 ml of 7 M aqueous sodium hydroxide, was shaken for half an hour, then it was treated with water, distilled, and handled as described under method(a). The distillation over potassium hydroxide pellets yielded 3.02 g (26.93 mmol) of 1. Little lower yields were obtained by quenching the reaction with water, or with ethanol, or with ethanolic solution of potassium hydroxide, rather than with aqueous sodium hydroxide.

Method(d). A mixture of 110 ml of a 0.5N ethereal solution of sodium ethoxide and 14.64 g (40.98 mmol) of methyltriphenylphosphonium bromide was stirred for 2 h under N_2, then treated dropwise with a solution of 5.81 g of crude 3-formyl-1,2,5-thiadiazole in 50 ml of ether and stirred for 3 h after the addition. The mixture was quenched with water and treated as described for method(a). 3.81 g (33.97 mmol) of 1 were collected after distillation over potassium hydroxide pellets.

Compound 1, treated with a 30% aqueous solution of cadmium chloride, gave a stable white precipitate. This solid complex regenerated compound 1 by distillation in aqueous suspension slightly acidified with sulphuric acid.

A 0.164 g sample (1.46 mmol) of 1 was treated by drops at room temperature with an aqueous solution 0.1M of potassium permanganate up to a persistent colour. The solution, by filtration, evaporation at reduced pressure, acidification with sulphuric acid and extraction with ether, yielded 0.185 g (1.42 mmol) of 1,2,5-thiadiazole-3-carboxylic acid which, after sublimation, exhibited melting point and IR spectrum coincident with those known.[10]

A solution of 0.83 g (7.40 mmol) of 1 in 2.5 ml of benzene was treated by drops with bromine up to persistent colour, then it was let to stay for 10 h. After decolourizing with active carbon and removing the solvent at reduced pressure, the residue was treated with anhydrous ether and crystallized by slow cooling at −70°. 1.96 g (7.21 mmol) of racemic 3-(1,2-dibromoethyl)-1,2,5-thiadiazole 5 were obtained which, after other three crystallizations from ether, melted in sealed tube at 22.5°. ν_{max} (film) 838, 793, 608, 520 (ring), 589 cm^{-1} (C-Br); δ (CCl_4) 8.57 (1H, s, ring proton), 5.45 (1H, q, aliphatic CH), 4.29 (1H, q, methylenic H_{trans}), 4.02 (1H, q, methylenic H_{gauche}); *geminal*, *gauche*, and *trans* coupling constants are 10.0, 5.5, and 9.8 cps respectively. Found: C, 17.84; H, 1.50; Br, 58.87; N, 10.23; S, 11.85. $C_4H_4Br_2N_2S$ requires: C, 17.67; H, 1.48; Br, 58.76; N, 10.30; S, 11.79%.

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