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VINYL TELLUROTHIOCARBAMATE

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Summary

The first organotellurothiocarbamate was prepared, isolated and characterized. The preparation involved quenching of a reaction between vinylmagnesium bromide and amorphous tellurium with dimethylthiocarbamoyl chloride.

Superconductivity [1] exhibited at high pressure by an organoselenium compound [tetramethyltetraselenafulvalene hexafluorophosphate, $(TMTSF)_2PF_6$] was recently confirmed and shown to be a bulk property of the crystal [2]. Because the unusual properties [3,4] of $(TMTSF)_2PF_6$ can be interpreted in terms of its solid state structure, particularly the selenium-selenium interactions [5], it could easily be postulated that the elusive $(TMTTeF)_2PF_6$ (tetramethyltetratellurafulvalene hexafluorophosphate) may in fact be a superconductor at atmospheric pressure, provided it retained the crystal structure of its selenium analog.

Pivotal to efficient syntheses of substituted selenafulvalenes are alkylations of selenacarbamates; the latter, we have shown, can be prepared efficiently from phosgene iminium chloride and hydrogen selenide. Unfortunately unlike other immonium ions [7], phosgene iminium chloride is reduced by hydrogen telluride [8]. it appeared, therefore, that a different strategy was necessary for the preparation of telluracarbamate (cf. Scheme 1).

Since compounds of type 1 were nonexistent [9], we considered that if 1a could be prepared, then the other analogs (R_1, R_2 = alkyl, aryl) could be prepared with greater ease because multiply substituted ethylenes are more stable than vinyls. Here we report on the first successful preparation of the title compound and some of its properties.

Since we did not expect 1a to be stable, we had to test the first step of the sequence (i.e. the Grignard plus chalcogen) with at least two chalcogens. As

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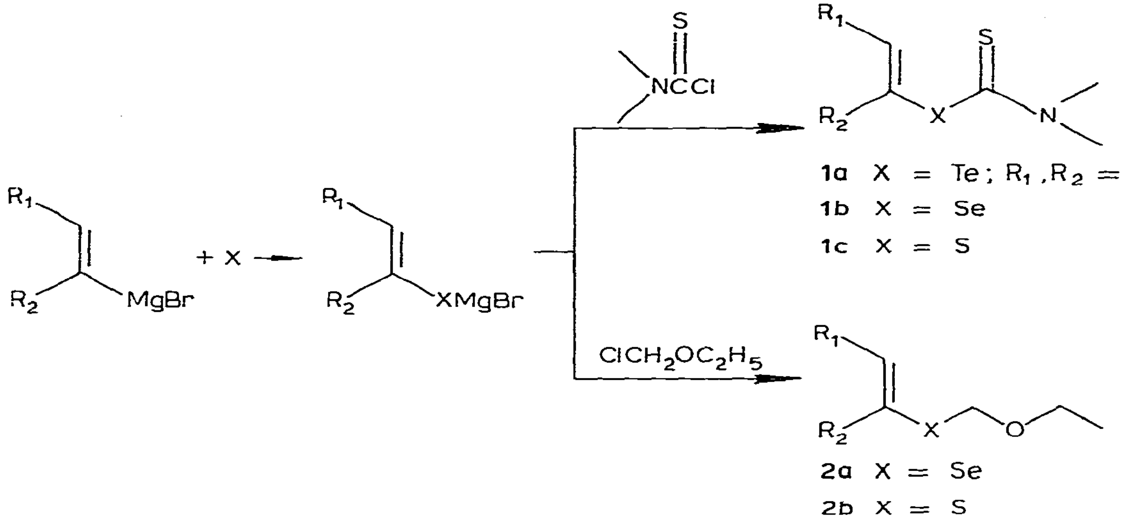
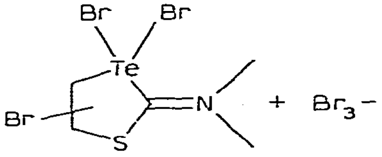
SCHEME 1



shown in Scheme 1 we used the strongly electrophilic chloromethyl ethyl ether to trap the vinyl chalcogenide. We were encouraged by the excellent yields and purity of product obtained in the trapping experiments (see Experimental section). Treatment of vinylmagnesium bromide in THF with tellurium at —78°C followed by dimethylthiocarbamoyl chloride and usual workup afforded **1a** in 72% yield as a low melting deep orange solid.

Vinyl tellurothiocarbamate is stable in the solid state under argon at room temperature and is soluble in all common organic solvents but is destroyed by acid (aqueous or nonaqueous, see below). Bromine reacts instantaneously to produce a slightly yellow insoluble solid whose elemental analysis is in agreement with **3** but confirmation of the hypothetical structure was (so far) impossible since "3" was unstable in solution and attempts to dehydrobrominate and reductively debrominate have met with failure (tellurium metal precipitated instantly when suspensions of "3" were treated with Ph_3P, Zn, $SnCl_2$ and $S_2O_5^{2-}$). Attempted cyclization of **1a** with HBF_4/HOAc also resulted in decomposition with concommitant tellurium precipitation.



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We have shown in this paper that vinyl tellurothiocarbamate can be prepared and that it is thermally (25°C) stable indefinitely (in an inert atmosphere). What remains to be shown is that the same synthetic procedure is applicable to the preparation of compound **1** ($R_1 = R_2 = CH_3$, etc.) which may be more stable to acid or dehalogenation of cyclized intermediates and that the bromination product is indeed **3** *.

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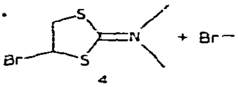
* K. Hiratani et al. [10] have found that vinyl dithiocarbamates cyclize cleanly with bromine to give **4** in excellent yield.



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Experimental

All reactions were performed under argon. NMR spectra were recorded with a Varian T-60 spectrometer. Elemental analyses were performed by Galbraith Laboratories.

Vinyl ethoxymethyl sulfide

Fifty ml of 1 *M* vinylmagnesium bromide in THF (Alfa) was cooled to —78°C (vinylmagnesium bromide forms a slurry) and treated with 1.6 g of sulfur. Immediate reaction took place (solution turned yellow). The mixture was stirred at —78°C for 1 h and 0°C for another hour (copious amount of yellow precipitate) followed by dropwise addition of 3.4 ml of chloromethyl ethyl ether (Aldrich). After 1.5 h at 0°C and 0.5 h at room temperature, the reaction mixture was poured into ice-dilute acetic acid and extracted three times with 150 ml of ether. The combined organic layer was washed three times with water, dried and evaporated to produce 1.6 g of a fetid yellow oil which needed no further purification (ms 118.198); NMR ($CDCl_3$, δ, ppm vs. TMS) 1.2 t, 3 H; 3.6 q, 2 H; 4.85 s, 2 H; 5.4 m, 2 H; 6.5 m, 1 H.

Vinyl ethoxymethyl selenide

The same procedure was used as above, except that for the workup, the reaction mixture was poured into ice-water and treated dropwise with glacial acetic acid until the milky magnesium hydroxide dissolved. A foul smelling yellow oil (73% yield) was obtained, ms 165.094, NMR ($CDCl_3$, δ, ppm vs TMS) 1.25 t, 3 H; 3.55 q, 2 H; 5.1 s, 2 H, 5.6 m, 2 H; 6.8 m, 1 H.

Vinyl tellurothiocarbamate

To 45.5 ml (0.5 mol) of vinylmagnesium bromide in THF (Alfa) at —78°C was added, all at once, 6.38 g (0.05 moles) of tellurium metal. After 1 h stirring at this temperature, the mixture was stirred at 0°C for another hour. The yellowish brown suspension which had formed was cooled to —78°C and treated with (dropwise) a solution of 6.18 g (0.05 mol) of dimethylthiocarbamoyl chloride in 25 ml of freshly distilled (from Na) THF. After addition was complete, the mixture was stirred at —78°C for 1/2 h at 0°C for 1 h and room temperature for another 1/2 h. The same work up as for the vinyl ethoxymethyl selenide (above) afforded 8.7 g (72% yield) of a deep orange-red solid (m.p. $\leqslant$25°C). Anal. Found: C, 24.97; H, 3.79; N, 5.67. calcd. for C_5H_6NSTe: C, 24.73; H, 3.74; N, 5.77%. NMR [$(CD_3)_2CO$, δ, ppm vs TMS] 3.4 d, 6 H; 5.75—6.35 m, 2 H; 7—7.5 m, 1 H. (IR, $CHCl_3$, cm^{-1}) 3040w, 3000s, 1670m, 1580m, 1498s, 1375s, 1240s, 1140s, 960vs, 920m, 845m, 660w.

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