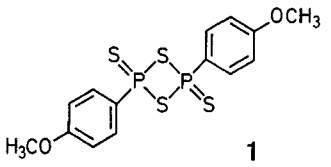
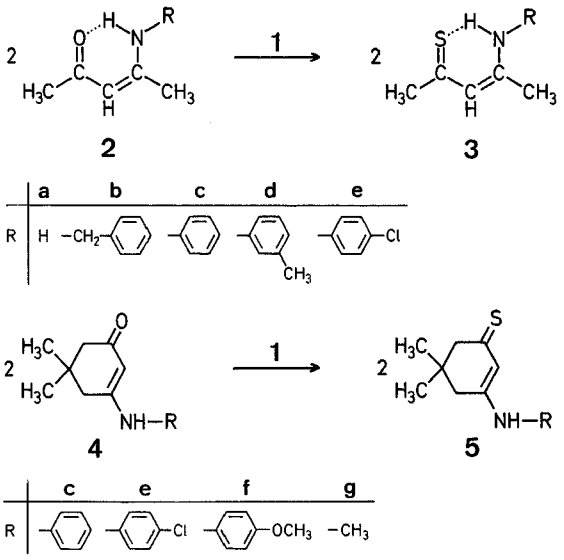


1

We have now used compound **1** for O/S exchange in vinylogous carboxamides **(2, 4)** having at least one H-atom on the N-atom to give the desired vinylogous thiocarboxamides **(3, 5)** in good yields.



The reaction is best carried out in dimethoxyethane at room temperature. The reaction solution becomes red and completely clear within 1 min and the temperature rises to 50–60° when no cooling is applied. Optimum results are obtained by keeping the reaction temperature at 20° and

Table 1. Vinylogous Thiocarboxamides **(3, 5)** from Vinylogous Carboxamides **(2, 4)**[a]

Product	Yield [%]	m.p. or b.p.	Molecular formula[b]	
3a	74	b.p. 101–102°/ 0.7 torr	C_5H_9NS	(115.2)[c]
3b[d]	42	m.p. 40°	$C_{12}H_{15}NS$	(205.3)
3c	60	m.p. 63°[e]	$C_{11}H_{13}NS$	(191.3)
3d	54	m.p. 48°	$C_{12}H_{15}NS$	(205.3)
3e[d]	20	m.p. 72°	$C_{11}H_{12}ClNS$	(225.7)
5c	58	m.p. 175°	$C_{14}H_{17}NS$	(231.4)
5e	80	m.p. 170°	$C_{14}H_{16}ClNS$	(265.8)
5f	69	m.p. 155–156°	$C_{15}H_{19}NOS$	(261.4)
5g	64	m.p. 115°	$C_9H_{15}NS$	(169.3)

[a] Compounds **2** and **4** were prepared according to Ref. [11].

[b] The microanalyses (except for **3a**) were in good agreement with the calculated values: C, ±0.17; H, ±0.14; N, ±0.10; S, ±0.11; Cl, ±0.15.

[c] Purification of **3a** by distillation of chromatography did not afford an analytically sufficiently pure product. The spectral data were in accord with Ref. [5], however.

calc.	C 52.13	H 7.87	N 12.16
found	52.57	7.71	11.74

[d] Reaction carried out in toluene at 50°.

[e] Ref. [5], m.p. 63–64°.

An Improved Preparation of Vinylogous Thiocarboxamides

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Vinylogous thiocarboxamides (2-amino-1-alkenyl thioketones) are important intermediates in the synthesis of various heterocyclic compounds. In addition, there is increasing interest[1,2,3] in the spectrometric data of this class of compounds. However, a simple method for the preparation of vinylogous thiocarboxamides in good yields and on a larger scale has hitherto not been available[4-8]. We report here a new and general method for the synthesis of these compounds.

The cyclic trithiophosphonic anhydrosulfide **1** (2,4-bis[4-methoxyphenyl]-2,4-dithioxo-P^V,P^V-1,3,2,4-dithiadiphosphetane) has recently been found to be an excellent sulfurizing agent[9,10].

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Table 2. Characteristic Spectral Data of Compounds **3** and **5**

Compound	I.R. (KBr or CCl_4) ν_{NH} [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$, 60 MHz) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$, 60 MHz) δ [ppm] (C=S)
3a	3280 (s), 2740 (br)	12.88, 6.83 (NH); 6.20 (CH)[a]	209.2
3b	2720 (br)	14.27 (NH); 6.13 (CH)	204.8
3c	2630 (br)	15.00[b] (NH); 6.28 (CH)	207.3
3d	2650 (br)	15.17 (NH); 6.15 (CH)	206.8
3e	2600 (br)	15.58 (NH); 6.33 (CH)	208.6
5c	3150 (s)	NH in the range of Ar H; 6.78 (CH)	222.4
5e	3190 (s)	NH in the range of Ar H; 6.72 (CH)	222.7
5f	3165 (s)	8.35 (NH); 6.62	219.4
5g	3180 (s)	6.60 (NH); 6.38 (CH)	217.6

[a] Cf. Ref. [5].
[b] Ref. [5], δ=15.01; 6.27 ppm.

using a reaction time of 5–15 min. Only small amounts of by-products are formed. Attempts to carry out the reaction in hexamethylphosphoric triamide (HMPT) at 80° or lower temperature gave unsatisfactory results. The preparation of compounds **3b** and **3e** in toluene at 50° afforded only moderate yields.

The spectrometric data listed in Table 2 show that the H-atom is bonded to the N-atom, i.e., that the products have the vinylogous thiocarboxamide structure with strong intramolecular H-bonding in **3a-e**.

Vinylogous Thiocarboxamides (3, 5; 2-Amino-1-alkenyl Thioketones); General Procedure:
In a 250 ml flask equipped with stirrer and calcium chloride tube, the vinylogous carboxamide (**2, 4**; 30 mmol) is placed in dry dimethoxyethane (100–150 ml). The solution is stirred for a few minutes and the flask is placed in a water bath at 20°. Then, the reagent **1** (6.47 g, 16 mmol) is added with stirring. Within 5–15 min, the mixture becomes clear and the color changes to deep orange or red. The mixture is then poured into water (300 ml) and extracted with chloroform (3 × 50 ml). The extract is dried with sodium sulfate and concentrated to ~20 ml. This liquid is filtered through a 25 × 5 cm column filled with silica gel/alumina (basic) (1/1) using chloroform as eluent. The solvent is evaporated and the crude product is recrystallized from tetrahydrofuran/hexane or aqueous ethanol.

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