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Hypervalent Iodine in Synthesis. Part 42: a General Method for Stereospecific Synthesis of *S*-Vinyl Dithiocarbonates†

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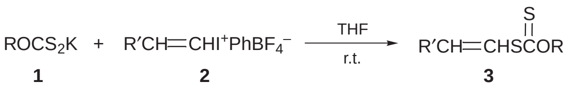
S-Vinyl dithiocarbonates are prepared by the reaction of potassium dithiocarbonates with vinyl(phenyl)iodonium tetrafluoroborates in THF in good yields.

Esters of dithiocarbonic acids (xanthates) play an important role in synthesis. For example, they can be used as intermediates for preparation of olefins *via* the Chugaev reaction[1,2] and can serve as convenient sources of carbon centered radicals in radical chain reactions.[3] They have also received much attention because of their biological activity.[4] The preparation of alkyl esters of dithiocarbonic acid is straightforward and can be prepared by the alkylation of salts of dithiocarbonic acids with alkyl halides.[5]

However, the method is not suitable for the preparation of *S*-vinyl dithiocarbonates because nucleophilic substitution at the vinyl carbon is difficult. Only a few *S*-vinyl dithiocarbonates have been reported and are usually prepared by the reaction of salts of dithiocarbonic acids with not readily available starting materials, such as triarylchloroallenes,[6] substituted thiiranes,[7] 4-bromo-3-phenylcyclobut-3-ene-1,2-dione,[8] azulene,[9] 1-cyanoalkane-1,2-dienes,[10] buta-1,3-diyne,[11] thianthrene[12] and unusual olefins.[13] In order to extend the member of *S*-vinyl dithiocarbonates and study their reactions and applications, a general method for preparation of the esters would be highly desirable.

Recently, our research interest has been in the chemistry of hypervalent iodine compounds. Because of the excellent leaving group ability of the phenyliodonium moiety alkenyl(phenyl)iodonium salts are highly reactive in vinylic nucleophilic substitutions and have been recognized to be useful as synthons of alkenyl cations,[14] which prompted us to examine their reaction with salts of dithiocarbonic acids for a simple and general method to prepare *S*-vinyl dithiocarbonates. Here we report the reaction of potassium dithiocarbonates **1** with vinyl(phenyl)iodonium salts **2** in THF which readily occurs over short times to afford *S*-vinyl dithiocarbonates **3** (Scheme 1).



$$\underset{\mathbf{1}}{\mathrm{ROCS_2K}} + \underset{\mathbf{2}}{\mathrm{R'CH{=}CHI^+PhBF_4^-}} \xrightarrow[\text{r.t.}]{\text{THF}} \underset{\mathbf{3}}{\mathrm{R'CH{=}CHS\overset{\overset{\large S}{||}}{C}OR}}$$

Scheme 1

Simple stirring of **1** with **2** in THF at room temperature for 5–15 min gave, after work-up and isolation, the desired *S*-vinyl esters **3** in good yields, as shown in Table 1. The products are characterized by IR, ^{1}H NMR and MS.

We selected (*E*)-[β-(phenyl)vinyl]phenyliodonium tetrafluoroborate and (*E*)-[β-(*n*-butyl)vinyl]phenyliodonium tetrafluoroborate[15] as representative examples of vinyl(phenyl)iodonium salts. We found that the reaction of (*E*)-[β-(phenyl)vinyl]phenyliodonium tetrafluoroborate with potassium dithiocarbonates was stereospecific and retention of configuration was observed for products **3**, probably *via* an addition–elimination mechanism.[16,17] However, complete inversion of configuration was obtained for the reaction of (*E*)-[β-(*n*-butyl)vinyl]phenyliodonium tetrafluoroborate with potassium dithiocarbonates which probably occurs *via* an S_N2 transition state.[17] The configurations of products **3** were assigned using ^{1}H NMR spectroscopy: *E*-isomers show a coupling constant *J* of 16 Hz *cf.* 9.6 Hz for the *Z*-isomers.

Table 1 *S*-Vinyl dithiocarbonates **3**

Product	R	R′	Reaction time/min	Configuration	Yield(%)
3a	Me	Ph	5	*E*	60
3b	Et	Ph	5	*E*	67
3c	Pr^n	Ph	10	*E*	62
3d	Bu^n	Ph	5	*E*	60
3e	$PhCH_2$	Ph	15	*E*	57
3f	Et	Bu^n	10	*Z*	67
3g	Pr^n	Bu^n	10	*Z*	74

In conclusion, we have presented a new and general method for the preparation of *S*-vinyl esters of dithiocarbonic acids. It has some advantages over other methods such as stereospecifcity, mild reaction conditions, simple procedure, accessible starting materials and good yields. Furthermore, the range of useful applications of vinyl(phenyl)iodonium salts as vinylating agents in organic synthesis has been extended.

Experimental

^{1}H NMR spectra were recorded on PMX-60 Spectrometer, using CCl_4 as the solvent with TMS as an internal standard. IR spectra were determined on PE-683 spectrophotometer. Mass spectra were measured on Finnigen MAT GC-MS mass spectrometer.

General Procedure for Synthesis of S-*Vinyl Dithiocarbonates* **3**.—A mixture of the appropriate potassium dithiocarbonate **1** (0.6 mmol) and vinyl(phenyl)iodonium tetrafluoroborate **2** (0.5 mmol) in THF (10 ml) was stirred at room temperature until the iodonium salt was completely consumed (monitored by TLC). Then, the mixture was diluted with water (15 ml) and extracted with dichloromethane (2 × 10 ml). The extract was washed with water (10 ml) and dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica gel plate using cyclohexane–ethyl acetate(9:1) as developer to give the pure *S*-vinyl ester of dithiocarbonic acid **3**.

(E)-O-*Methyl* S-2-*Phenylvinyl Dithiocarbonate* **3a**. Oil; δ_H 4.23 (3H, s), 6.73 (1H, d, $J = 16$ Hz), 7.00–7.50 (6H, m); ν_{max}/cm^{-1} (film) 3040, 1230, 1070, 945, 730, 680; *m/z* 210 (M^+, 34.9), 91 (100%).

(E)-O-*Ethyl* S-2-*Phenylvinyl Dithiocarbonate* **3b**. Oil; δ_H 1.51 (3H, t, $J = 7$ Hz); 4.80 (2H, q, $J = 7$ Hz); 6.89 (1H, d, $J = 16$ Hz), 7.30–7.60 (6H, m); ν_{max}/cm^{-1} (film) 3040, 1230, 1050, 1040, 940, 730, 680; *m/z* 224 (M^+, 15.9), 135 (100%).

(E)-O-n-*Propyl* S-2-*Phenylvinyl Dithiocarbonate* **3c**. Oil; δ_H 1.07 (3H, t, $J = 7$ Hz), 160–2.10 (2H, m), 4.62 (2H, t, $J = 7$ Hz), 6.73 (1H, d, $J = 16$ Hz), 7.17–7.56 (6H, m); ν_{max}/cm^{-1} (film) 3040, 1270, 1230, 1040, 1030, 940, 730, 680; *m/z* 238 (M^+, 6.21), 135 (100%).

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(E)-O-n-*Butyl* S-2-*Phenylvinyl Dithiocarbonate* **3d**. Oil; δ_H 0.98 (3H, t, $J = 6$ Hz), 1.17–1.95 (4H, m), 4.73 (2H, t, $J = 6$ Hz), 6.87 (1H, d, $J = 16$ Hz), 7.30–7.50 (6H, m); ν_{max}/cm^{-1} (film) 3010, 1270, 1230, 1050, 1030, 945, 735, 680; m/z 252 (M^+, 0.47), 205 (100%).

(E)-O-*Phenylnethyl* S-2-*Phenylvinyl Dithiocarbonate* **3e**. Oil; δ_H 3.46 (2H, s), 6.57 (1H, d, $J = 16$ Hz), 6.98–7.40 (11H, m); ν_{max}/cm^{-1} (film) 3040, 1270, 1230, 1070, 1050, 950, 730, 690; m/z 286 (M^+, 15.1), 91 (100%).

(Z)-O-*Ethyl* S-1-*Hexenyl Dithiocarbonate* **3f**. Oil; δ_H 0.93 (3H, t, $J = 7$ Hz), 1.15–1.65 (7H, m), 1.95–2.40 (2H, m), 4.65 (2H, *q*, $J = 7$ Hz), 5.57–6.03 (1H, m), 6.63 (1H, d, $J = 9.6$ Hz); ν_{max}/cm^{-1} (film) 3020, 1220, 1050, 690; m/z 204 (M^+, 100%).

(Z)-O-n-*Propyl* S-1-*Hexenyl Dithiocarbonate* **3g**. Oil; δ_H 0.92 (3H, t, $J = 7$ Hz), 1.02–1.62 (9H, m), 1.97–2.40 (2H, m), 4.57 (3H, t, $J = 7$ Hz), 5.60–6.10 (1H, m), 6.68 (1H, d, $J = 9.6$ Hz); ν_{max}/cm^{-1} (film) 3020, 1220, 1060, 1040, 690; m/z 218 (M^+, 100%).

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