A Convenient Synthesis of 2-Arylvinyl and 4-Aryl-1,3-butadienyl Arenedithiocarboxylates

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Vinyl dithiocarboxylates have attracted considerable attention because of their potential usefulness as synthetic intermediates[1,2,3]. However, the known synthetic methods are concerned with vinyl alkanedithioates and general methods have

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not been developed. We report here a new practical method for the synthesis of the title compounds **7** and **8**, via the new phosphonium salts, phosphoniomethyl iodide dithiocarboxylates **3**[4].

The phosphonium salts **3** are prepared by addition of piperidinium arenedithiocarboxylates[5] **1** to a chloroform suspension of iodomethyltriphenylphosphonium iodide[6] **(2)** at room temperature (Table 1). Treatment of the salts **3** suspended in tetrahydrofuran with an equimolar amount of potassium *t*-butoxide at −75 °C under argon gave a deep purple colored solution of the ylid **4**. Subsequent addition of an aryl aldehyde **5** and warming of the mixture to 0 °C gave, after work up, the crystalline arylvinyl arenedithiocarboxylates **7**. Similar treatment of **4** with cinnamaldehydes **6** gave the 4-aryl-1,3-butadienyl arenedithiocarboxylates **8**.

To the best of our knowledge, this procedure is the first general method for the preparation of the crystalline compounds **7** and **8** (Table 2).

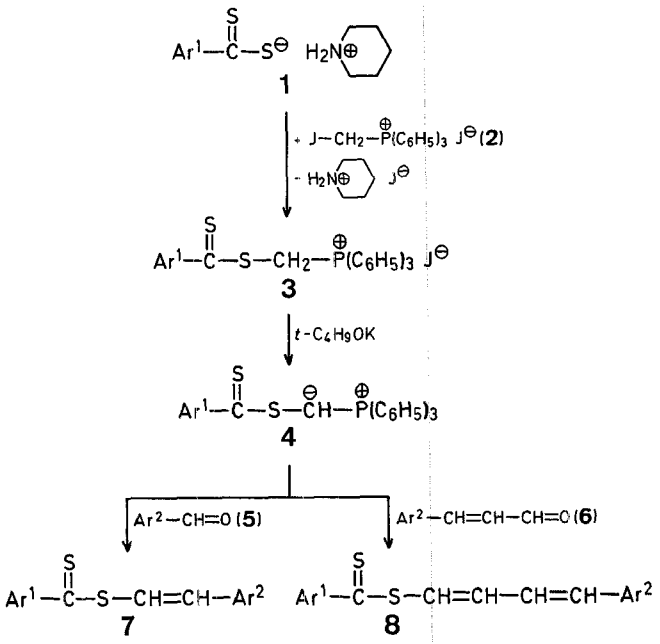

Table 1. Yields and Physical Properties of Phosphoniomethyl Dithiocarboxylate Iodides **(3)**

Product No.	Ar^1	Yield[a] [%]	m.p. [°C]	Molecular Formula[b]	I.R. (KBr) $\nu_{C=S}$ [cm^{-1}]	U.V. and Vis. (CH_2Cl_2) λ_{max}, [nm] ($\log\varepsilon$)	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
3a	C_6H_5	46	174–178°	$C_{26}H_{22}S_2PJ$ (556.5)	1230, 1040	308 (4.37); 483 (2.34)	7.20–8.20 (m, 20H, H_{arom}); 5.90 (d, 2H, CH_2)
3b	4-H_3C—C_6H_4	72	179–182°	$C_{27}H_{24}S_2PJ$ (570.5)	1240, 1040	321 (4.38); 487 (2.44)	7.40–8.15 (m, 19H, H_{arom}); 5.85 (d, 2H, CH_2); 2.42 (s, 3H, CH_3)
3c	4-H_3CO—C_6H_4	63	202–205°	$C_{27}H_{24}OS_2PJ$ (586.5)	1250, 1045	360 (4.36); 483 (2.53)	7.25–8.05 (m, 19H, H_{arom}); 6.08 (d, 2H, CH_2); 3.79 (s, 3H, CH_3O)
3d	4-Cl—C_6H_4	39	171–175°	$C_{26}H_{21}S_2PClJ$ (590.9)	1230, 1045	318 (4.42); 488 (2.44)	7.20–8.20 (m, 19H, H_{arom}); 5.85 (d, 2H, CH_2)

[a] Yield of isolated products.

[b] Satisfactory microanalyses obtained: C ±0.14, H ±0.05.

Table 2. 2-Arylvinyl and 4-Aryl-1,3-butadienyl Arenedithiocarboxylates **7** and **8**

Product No.	Ar^1	Ar^2	Yield[a] [%]	m.p. [°C] (solvent)	Molecular Formula[b]	I.R. (KBr) $\nu_{C=S}$ [cm^{-1}]	U.V. and Vis. (CH_2Cl_2) λ_{max} [nm] ($\log\varepsilon$)	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	M.S. (70 eV) *m/e* (M^+)
7a	C_6H_5	4-O_2N—C_6H_4	45	135–138° (C_2H_5OH)	$C_{15}H_{11}NO_2S_2$ (301.3)	1245, 1045	311 (4.42); 512 (2.38)	6.6–8.2 (m, 11H)	301
7b	4-H_3C—C_6H_4	C_6H_5	75	50–51°[c]	$C_{16}H_{14}S_2$ (270.4)	1240, 1045	269 (4.21); 328 (4.32); 503 (2.40)	2.35 (s, 3H); 6.8–8.2 (m, 11H)	270
7c	4-H_3C—C_6H_4	4-O_2N—C_6H_4	89	122–128°[c]	$C_{16}H_{13}NO_2S_2$ (315.4)	1250, 1052	332 (4.43); 507 (2.34)	2.35 (s, 3H); 6.75–8.4 (m, 10H)	315
7d	4-H_3CO—C_6H_4	C_6H_5	39	49–50°[c]	$C_{16}H_{14}OS_2$ (286.4)	1245, 1040	249 (4.19); 269 (4.20); 356 (4.47); 503 (2.53)	3.85 (s, 3H); 6.75–8.3 (m, 11H)	286
7e	4-H_3CO—C_6H_4	4-O_2N—C_6H_4	56	166–168° (C_2H_5OH)	$C_{16}H_{13}NO_3S_2$ (331.4)	1255, 1040	367 (4.58); 504 (2.57)	3.55 (s, 3H); 7.35–8.85 (m, 10H)	331
8a	4-H_3CO—C_6H_4	2-O_2N—C_6H_4	94	96–100° (CH_2Cl_2/C_2H_5OH)	$C_{18}H_{15}NO_3S_2$ (357.5)	1250, 1040	361 (4.52); 491 (2.72)	3.85 (s, 3H); 6.5–8.3 (m, 12H)	357[d]
8b	4-H_3CO—C_6H_4	4-O_2N—C_6H_4	88	192–194° (CH_2Cl_2/C_2H_5OH)	$C_{18}H_{15}NO_3S_2$ (357.5)	1240, 1040	245 (4.29); 365 (4.55); 513 (2.96)	3.90 (s, 3H); 6.65–8.25 (m, 12H)	357[d]

[a] Yield of pure, isolated product.

[b] Satisfactory microanalyses obtained: C ±0.25, H ±0.09, N ±0.25, S ±0.20; exception: **7a**, C −0.5.

[c] Recrystallization not necessary.

[d] At 20 eV.

Triphenylphosphoniomethyl *p*-Toluenedithiocarboxylate Iodide (3b); Typical Procedure:

Piperidinium *p*-toluenedithiocarboxylate (**1**, 0.51 g, 2.0 mmol) is added to a suspension of iodomethyltriphenylphosphonium iodide (**2**; 1.10 g, 2.0 mmol) in chloroform (60 ml). The mixture is stirred for 4 h at room temperature. The resulting homogeneous solution is washed with water (3 × 50 ml) and dried with sodium sulfate. After removal of the solvent, the residue is added dropwise with stirring to dry ether (200 ml) at 0 °C to give **3b** as orange precipitates; yield: 0.82 g (72%). Pure **3b** is obtained by recrystallization from ethyl acetate/dichloromethane; m.p. 179–182 °C.

$C_{27}H_{24}JPS_2$	calc.	C 58.85	H 4.24
(570.5)	found	56.89	4.19

2-(4-Nitrophenyl)-vinyl *p*-Toluenedithiocarboxylate (7c); Typical Procedure:

To the salt **3b** (0.57 g, 1.0 mmol) suspended in dry tetrahydrofuran (30 ml) is added potassium *t*-butoxide (0.112 g, 1.0 mmol) under argon at −75 °C. The mixture is stirred at that temperature for 30 min. Then, 4-nitrobenzaldehyde (**5**; 0.151 g, 1.0 mmol) is added and the mixture gradually warmed to 0 °C within 3 h. The mixture is poured into water (50 ml), extracted with ether (3 × 50 ml), and the extract dried with sodium sulfate. After removal of the solvent, the residue is chromatographed on silica gel (benzene/*n*-hexane = 1 : 10 as eluent) to give **7c** as red crystals; yield: 0.281 g (89%). Pure **7c** is obtained by recrystallization from ethanol; m.p. 122–128 °C.

$C_{16}H_{13}NO_2S_2$	calc.	C 60.93	H 4.15
(315.4)	found	61.12	4.15

4-(2-Nitrophenyl)-1,3-butadienyl *p*-Toluenedithiocarboxylate (8a); Typical Procedure:

Similarly to the synthesis of **7c**, from the salt **3c** (0.586 g, 1.0 mmol) and 2-nitrocinnamaldehyde (**6**; 0.177 g, 1.0 mmol) is obtained 4-(2-nitrophenyl)-1,3-butadienyl *p*-toluenedithiocarboxylate **(8a)** as red crystals; yield: 0.335 g (94%). A pure sample is recrystallized from dichloromethane/ethanol: m.p. 96–100 °C.

$C_{18}H_{15}NO_3S_2$	calc.	C 60.48	H 4.23	N 3.92	S 17.94
(357.5)	found	60.35	4.22	3.98	17.65

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[1] M. Saquet, T. Thuillier, *Tetrahedron Lett.* **21**, 2165 (1980).

[2] G. Levesque, A. Mahjour, *Tetrahedron Lett.* **21**, 2247 (1980).

[3] M. Schoufs, J. Meijer, P. Vermeer, L. Brandsma, *Synthesis* **1978**, 439.

[4] We have previously reported the corresponding acylated salts: $[Ar—CS_2—CH(CO—C_6H_5)\overset{\oplus}{P}(C_6H_5)_3]Ar—CS_2^{\ominus}$; S. Kato, S. Imamura, M. Mizuta, *Int. J. Sulfur Chem.* [A] **2**, 283 (1972), and the nitrogen analogues, aminomethyl dithiocarboxylates; M. Ishida, S. Kato, M. Mizuta, *Z. Naturforsch.* [b] **36**, 1047 (1981).

[5] S. Kato, T. Mitani, M. Mizuta, *Int. J. Sulfur Chem.* **8**, 359 (1973).

[6] H. Hellmann, J. Bader, *Tetrahedron Lett.* **1961**, 724.

[7] Compounds **7b–d** were chromatographed on silica gel (benzene/*n*-hexane = 1 : 10 as eluent); **8a** and **8b** were also chromatographed on silica gel (benzene as eluent).

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