Polyvalent Iodine in Synthesis; 3. An Efficient Method for the Synthesis of Aryl Arenedithiocarboxylates

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A new method for the synthesis of aryl arenedithiocarboxylates consists of the *S*-arylation of sodium arenedithiocarboxylates with diaryliodonium chlorides or bromides in *tert*-butyl alcohol.

Following our finding that diaryliodonium salts are efficient electrophilic arylating agents for dithiocarbamic acid salts,[1] we investigated the possibility of extending this *S*-arylation reaction to arenedithiocarboxylic acid salts. Such a reaction would provide a useful route to aryl arenedithiocarboxylates (**3**), a compound class which is of interest as regards structure as well as applicability in organic synthesis and in industry.[2]

A number of methods have been reported for the synthesis of aryl dithiocarboxylates, e. g., the *S*-thioacylation of thiophenols with thioacyl chlorides,[3] bis(thioacyl) sulfides,[4] or thioacyl diphenylphosphinodithioates,[5] treatment imidothioic esters with hydrogen sulfide,[6] the Friedel-Crafts reaction between aromatic substrates and carbonochloridodithioic esters,[7] transesterification between carboxymethyl dithiocarboxylates with thiophenols,[8] thiation of carboxylic esters or thiocarboxylic esters,[9-11] treatment of halomagnesium or sodium dithiocarboxylates with *S*-phenyl carbonochloridothioate.[12] However, all these methods implicate either toxic and hazardous reagents or multistep procedures and uncommon starting materials, thus limiting a general simple access to aryl dithiocarboxylates.

Table. Aryl Arenedithiocarboxylates 3 Prepared

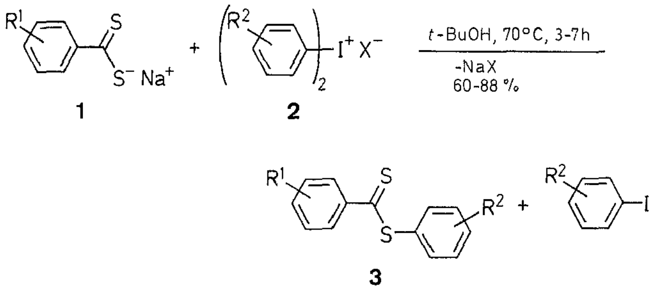
Product	X in 2	Reaction Time (h)	Yield[a] (%)	Lit. Yield	mp (°C)	Molecular Formula[b] or Lit. mp (°C)	^{1}H-NMR ($CDCl_3$/TMS) δ
3a	Cl	4	65	60[6,7,12]	59–60	60–62[6] 59–60[7] 60–61[8] 63–64[15]	7.26–7.54 (m, 8H); 8.03–8.18 (m, 2H)
3b	Br	7	73	34[7]	58–59	58–59.5[7]	2.38 (s, 3H); 7.28–7.57 (m, 7H); 7.97–8.12 (d, 2H)
3c	Cl	6	77		64–66	$C_{13}H_9ClS_2$ (284.7)	7.26–7.46 (m, 7H); 8.00–8.18 (d, 2H)
3d	Br	3	64		79–81	$C_{13}H_9NO_2S_2$ (275.2)	7.26–8.45 (m, 9H)
3e	Cl	4	81	95[7] 90[4]	63–64	83–84[7] 62–63[4] 77–79[5]	2.39 (s, 3H); 7.10–7.23 (d, 2H); 7.46 (s, 5H); 7.93–8.06 (d, 2H)
3f	Br	7	75		94–96	$C_{15}H_{14}S_2$ (258.3)	2.36 (s, 3H); 2.39 (s, 3H); 7.10–7.30 (m, 6H); 7.92–8.06 (d, 2H)
3g	Cl	6	68		100–102	$C_{14}H_{11}ClS_2$ (278.7)	2.37 (s, 3H); 7.15–7.43 (m, 6H); 7.97–8.10 (d, 2H)
3h	Br	3	69		77–79	$C_{14}H_{11}NO_2S_2$ (289.3)	2.40 (s, 3H); 7.13–8.38 (m, 8H)
3i	Cl	4	65		43–44	$C_{14}H_{12}S_2$ (244.3)	2.40 (s, 3H); 7.18–7.54 (m, 9H)
3j	Br	7	60		43–45	$C_{15}H_{14}S_2$ (258.3)	2.40 (s, 6H); 7.15–7.50 (m, 8H)
3k	Br	4	88		77–78	$C_{14}H_{11}NO_2S_2$ (289.3)	2.43 (s, 3H); 7.20–7.40 (m, 4H). 7.60–7.84 (m, 2H); 8.26–8.44 (m, 2H)
3l	Br	5	79		95–97	$C_{18}H_{14}S_2$ (294.3)	2.42 (s, 3H); 7.36–8.65 (m, 11H)

[a] Yield of isolated analytically pure product, based on **1**.

[b] Satisfactory microanalyses obtained: C ± 0.23; H ± 0.10.

Herein we report a simple and efficient method for the synthesis of aryl arenedithiocarboxylates **3** by direct *S*-arylation of sodium arenedithiocarboxylates **1** with diaryliodonium salts **2**.

Our initial investigation carried out with bromomagnesium 4-methylbenzenedithiocarboxylate and diphenyliodonium chloride resulted in a rather low yield (~30%) of the expected phenyl 4-methyldithiobenzoate (**3e**). The low reactivity of the bromomagnesium dithiocarboxylate was assumed to be due to insufficient ionic properties. Replacement of the bromomagnesium salt by the sodium salt increased the reactivity, as expected; thus, stirring the sodium arenedithiocarboxylates **1** with the appropriate diaryliodonium salts **2** in *tert*-butyl alcohol at 70°C gave, after work-up, the desired aryl arenedithiocarboxylates **3** in good yields (Table).



3	R^1	R^2	3	R^1	R^2
a	H	H	**g**	4-CH_3	4-Cl
b	H	4-CH_3	**h**	4-CH_3	3-NO_2
c	H	4-Cl	**i**	2-CH_3	H
d	H	3-NO_2	**j**	2-CH_3	4-CH_3
e	4-CH_3	H	**k**	2-CH_3	3-NO_2
f	4-CH_3	4-CH_3	**l**	3,4-$(CH)_4$	4-CH_3

The products **3** were characterized by spectral and analytical means as summarized in the Table.

All melting points are uncorrected. ^{1}H-NMR spectra were recorded at 60 MHz on an EM-360 spectrometer.

The sodium arenedithiocarboxylates **1** were prepared from the corresponding arylmagnesium halides and CS_2[13] in THF, acidification of the reaction mixture, and addition of NaOH/H_2O. The diaryliodonium salts **2** were prepared by standard procedures.[14]

Aryl Arenedithiocarboxylates 3; General Procedure:

To the stirred red solution of the sodium arenedithiocarboxylate **1** (10 mmol) in *t*-BuOH (15 mL) is slowly added the appropriate iodonium salt **2** (10 mmol). The resultant mixture is stirred at 70°C for the time given in the Table. The solvent is removed under reduced pressure, H_2O (15 mL) is added to the residue, and the resultant mixture is extracted with CH_2Cl_2 (3 × 10 mL). The extract is washed with H_2O (10 mL) and dried ($MgSO_4$). The solvent is removed, hexane (10 mL) is added to the residue, and the product is allowed to crystallize in a refrigerator overnight. The crude product is isolated and recrystallized from benzene/hexane.

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