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Copper(I) Salt Promoted Reactions of Sulfur Nucleophiles with Vinyl Bromides. Simple and Straightforward Preparations of S-Vinyl Thiobenzoates and S, S'-Vinylidene Bisthiobenzoates

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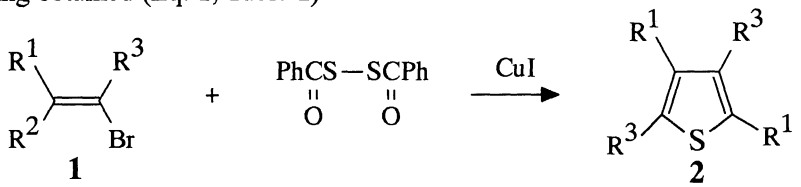
Copper(I) salt promoted reaction of vinyl bromides with dibenzoyl disulfide in hot aprotic polar solvent produced thiophene derivatives in moderate yields, while the corresponding reaction with sodium thiobenzoate led to S-vinyl thiobenzoates in good yields.

In a previous communication,[1] we reported that aryl vinyl sulfides can be prepared in good yields by the copper(I) salt promoted reaction of vinyl bromides with diaryl disulfides in aprotic polar solvents. However, when diaryl disulfide was replaced by dibenzoyl disulfide, a novel mode of reaction took place to give 2,4-diarylthiophene in a moderate yield together with N,N-dimethylbenzamide, no expected S-alkenyl thiobenzoate being obtained (Eq. 1; Table 1).



(1)

When 1-bromo-2-phenylethene was reacted with bis(4-methylbenzoyl) disulfide, only 2,4-diphenylthiophene was obtained and no 4-methylphenyl moiety was incorporated into thiophene nucleus, which clearly demonstrates that two aryl groups on the thiophene ring were derived not from dibenzoyl disulfide but from the olefinic portion. A possible intermediacy of acetylenic compounds[2,3] in these reactions was ruled out, because thiophenes were not produced from the reaction of phenylacetylene with dibenzoyl disulfide; bis(2-phenylethenyl) sulfide was the only product obtained in 30% isolated yield.

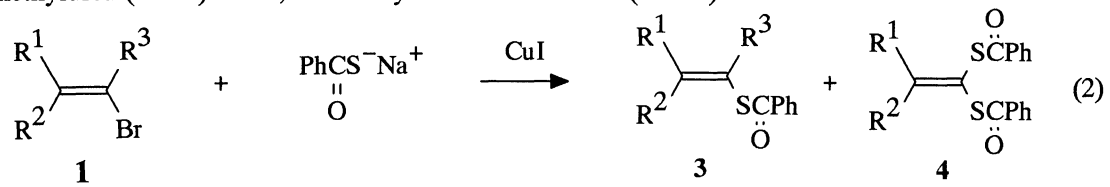
When 1-bromo-1-octene was reacted similarly, no thiophene was produced but S-(1-octenyl) thiobenzoate was isolated in 37% yield. From these observations we first suspected a possible participation of S-vinyl thiobenzoate (**3**) in the thiophene-forming reaction. However, this proved not to be the case, since no thiophene was obtained from the reaction of S-(2-phenylethenyl) thiobenzoate with 1-bromo-2-phenylethene under the same conditions.

Copper(I) iodide was essential for these transformations; without this or with copper(II) salts such as copper(II) bromide and copper(II) sulfide as catalyst, starting materials were recovered almost unchanged. Attempted reaction of copper thiobenzoate with 1-bromo-2-phenylethene in HMPA also resulted in the recovery of starting materials.

In a recent communication, Nakayama and coworkers reported[3] the thiophene ring formation from

elemental sulfur and acetylenic compounds at elevated temperatures. However, the mode of the reaction is quite different from ours; a mixture of 2,4- and 2,5-diphenylthiophene were obtained along with 2,5- and 2,6-diphenyl-1,4-dithiins in their reaction, while only 2,4-diarylthiophene was formed in our reaction.

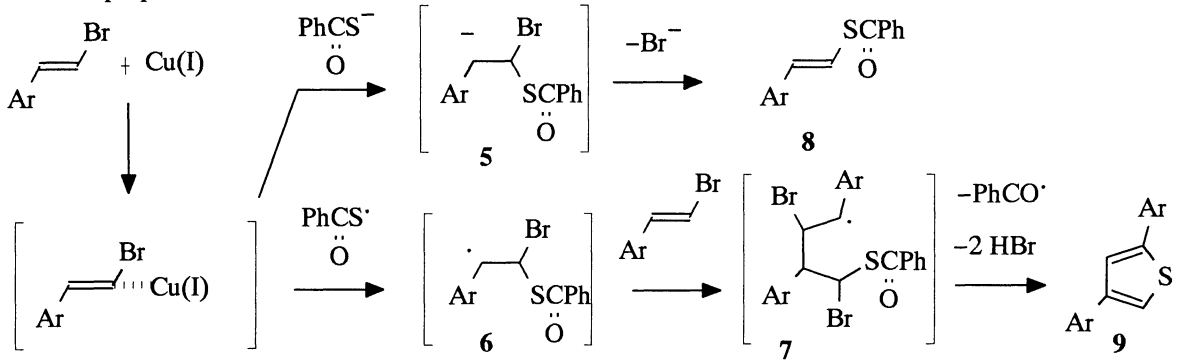
When sodium thiobenzoate was reacted with vinyl bromides or vinylidene dibromides, substitution reaction occurred to produce S-vinyl thiobenzoate (**3**) or S,S'-vinylidene bisthiobenzoates (**4**) in good yields (Eq. 2; Table 2).[4] The substitution reaction proceeded smoothly not only in HMPA but also in 1,1,3,3-tetramethylurea (TMU) and 1,3-dimethyl-2-imidazolidone (DMIZ).



1 **3** **4**

A tentative mechanistic proposal which may account for our observations is depicted in Scheme 1. Recent works concerning the copper salt promoted nucleophilic aromatic substitution reactions assume the aggregate formation between the copper ion and the aryl moiety as the initial stage of the reaction. The next step will be a partial transfer of electron density from the copper ion to the aryl moiety, which will weaken the carbon-bromine bond when it is situated in the σ^*-orbital.[5] We may safely apply a similar idea to the activation of nonactivated vinyl halides described herein. Thus, sodium thiobenzoate can undergo the addition/elimination reaction with vinyl halides to give the corresponding vinyl thiobenzoates (**8**). On the other hand, dibenzoyl disulfide releases the benzoylthio radical upon heating at high temperatures. This radical will add to vinyl halide to give a benzyl radical (**6**), which is then trapped by another molecule of vinyl halide and cyclizes to form thiophene derivative **9** after the expulsion of benzoyl radical and two molecules of hydrogen bromide. The major reason for the observed difference in the mode of reactions of sodium thiobenzoate and of dibenzoyl disulfide would be attributed to the difference in stability of the intermediate anion **5** and radical species **6**; the benzyl radical **6** would have a life time enough to be trapped by another molecule of olefin to form the second radical species **7**, which will cyclize and aromatize to produce 2,5-diarylthophene (**9**). In contrast, the β-bromo anion **5** will undergo a facile β-elimination of bromine atom, giving the expected vinylic compound **8**.

S-Vinyl thiobenzoates are useful as a precursor for various sulfur-containing compounds, but their synthesis needs somewhat tedious procedures.[6] And none of these known methods are apparently applicable to the preparation of *gem*-di(benzoylthio)vinylic compounds. The present method provides a simple direct way for their preparation.



5 **8** **6** **7** **9**

Scheme 1.

Table 1. Thiophene Derivatives (**2**) from Vinyl Bromides (**1**) and Dibenzoyl Disulfide

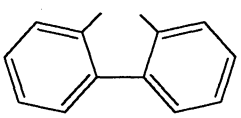
Run	R^1	R^2	R^3	Solvent[a]	Yield /%[b]	Mp θm/°C
1	C_6H_5	H	H	HMPA	40	121-124
2	C_6H_5	H	H	DMF	10	121-124
3	C_6H_5	H	H	DMSO	0	-------
4	C_6H_5	H	H	HMPT	0	-------
5	$4\text{-}CH_3OC_6H_4$	H	H	HMPA	57	215-216
6	$4\text{-}CNC_6H_4$	H	H	HMPA	(51)[c]	-------
7	C_6H_5	H	C_6H_5	HMPA	61	189-191

a) HMPA = hexamethylphosphoric triamide, DMF = dimethylformamide, DMSO = dimethylsulfoxide, and HMPT = hexamethylphosphorous triamide.

b) Yields refer to isolated compounds and were not optimized.

c) Extensive decomposition took place during attempted purification for analytical purpose.

Table 2. S-Vinyl Thiobenzoates (**3**) and S,S'-Vinylidene Bisthiobenzoates (**4**) from the Corresponding Bromides (**1**)

Run	**1** R^1	**1** R^2	**1** R^3	Solvent[a]	Yield /%[b] **3**	Yield /%[b] **4**	Mp θm/°C
1	C_6H_5	H	H	TMU	72	--	103-103.5
2	$4\text{-}CH_3OC_6H_4$	H	H	TMU	74	--	215-216
3	(C_6H_5)[c]	(H)[c]	C_6H_5	TMU	72	--	115-116
4	$CH_3(CH_2)_5$	H	H	TMU	66		oil
5	$-(CH_2)_5-$		Br	HMPA	--	80	143-144
6	$-(CH_2)_5-$		Br	TMU	--	82	143-144
7	$-(CH_2)_5-$		Br	DMIZ	--	44	143-144
8	$-(CH_2)_4-$		Br	TMU	--	66	129-130
9			Br	TMU	--	34	62-65

a) TMU = tetramethylurea and DMIZ = 1,3-dimethyl-2-imidazolidone.

b) Yields refer to the isolated compounds and were not optimized.

c) E/Z ratio was not determined.

References

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3) J. Nakayama, R. Yomoda, and M. Hoshino, *Heterocycles*, **26**, 2215 (1987).

4) The General procedure for synthesis of vinyl thiobenzoates is as follows: A mixture of vinyl bromide (1 mmol), copper iodide (2 mmol) and dry TMU (2 ml) was heated at 120 °C under a nitrogen atmosphere. To this mixture was added dropwise over 1 h a TMU solution (2 ml) of sodium thiobenzoate (1.2 mmol) prepared from thiobenzoic acid and sodium hydride. When the starting bromide was consumed completely, the mixture was cooled to room temperature and 10% aq. HCl solution saturated with NaCl was added. The product was extracted with diethyl ether, dried over Na_2SO_4, evaporated, and purified by passing through a silica-gel column using hexane/CH_2Cl_2 as eluent. Spectral and analytical data of some representative products are as follows: S-(2-Phenylethenyl) thiobenzoate; colorless crystals. ^{1}H NMR ($CDCl_3$) δ = 6.87 (d, J=16.5 Hz, 1H) and 7.17-8.05 (m, 11H). IR (KBr) 1680 and 1210 cm^{-1}. MS (EI, 20 eV) m/z (rel. intensity) 240 (M^+, 8) and 105 (100). Anal. Found: C, 75.32; H, 5.10%. Calcd for $C_{15}H_{12}OS$: C, 74.97; H, 5.03%. S-[2-(4-Methoxyphenyl)ethenyl] monothiobenzoate; colorless crystals. ^{1}H NMR ($CDCl_3$) δ = 3.76 (s, 3H of one isomers), 3.78 (s, 3H of one isomers), 6.75 (d, J=11 Hz, 1H of one isomers), 6.74-7.62 (m, 9H), 7.05 (d, J=11 Hz, 1H of one isomers). IR (KBr) 1665 and 1210 cm^{-1}. MS (EI, 20 eV) m/z (rel. intensity) 270 (M^+, 1) and 105 (100). Anal. Found: C, 71.07; H, 5.30%. Calcd for $C_{16}H_{14}O_2S$: C, 71.09; H, 5.22%. S-(1-Octenyl) thiobenzoate; colorless liquid. ^{1}H NMR ($CDCl_3$) δ = 0.85-0.91 (m, 3H), 1.29-1.44 (m, 8H), 2.15-2.27 (m, 2H), 5.94 (dt, J = 7 and 9 Hz, vinyl proton of Z isomer), 6.02 (dt, J = 7 and 15 Hz, vinyl proton of E isomer), 6.61(dt, J = 1.5 and 15 Hz, vinyl proton of E isomer), 6.74 (dt, J=1.5 and 9 Hz, vinyl proton of Z isomer), 7.41-7.49 (m, 2H), 7.54-7.61 (m, 1H), and 7.92-8.01 (m, 2H). IR (NaCl) 1665 and 1200 cm^{-1}. MS (EI, 20 eV) m/z (rel intensity) 248 (M^+, 2) and 105 (100). Anal. Found: C, 72.63; H, 8.12%. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.10%. S,S-(1,4-Butanediyl)vinylidene bis(thiobenzoate); colorless crystals. ^{1}H NMR ($CDCl_3$) δ = 1.78-1.84 (m, 4H), 2.60-2.65 (m, 4H), 7.40-8.00 (m, 10H). IR (KBr) 1680 and 1205 cm^{-1}. MS (EI, 20 eV) m/z (rel intensity) 354 (M^+, 0.5) and 105 (100). Anal. Found: C, 67.94; H, 5.22%. Calcd for $C_{20}H_{18}O_2S_2$: C, 67.76; H, 5.12%. S,S-(1,5-Pentanediyl)vinylidene bis(thiobenzoate); colorless crystals. ^{1}H NMR ($CDCl_3$) δ = 1.60-1.70 (m, 6H), 2.64-2.68 (m, 4H), 7.4-7.7 (m, 6H), 7.9-8.0 (m, 4H). IR (KBr) 1675 and 1200 cm^{-1}. MS (CI, 70 eV) m/z (rel intensity) 369 (M^++1, 2) and 263 (100). Anal. Found: C, 68.04; H, 5.67%. Calcd for $C_{21}H_{20}O_2S_2$: C, 68.44; H, 5.47%.

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