A highly efficient carbon–sulfur bond formation reaction via microwave-assisted nucleophilic substitution of thiols to polychloroalkanes without a transition-metal catalyst

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Abstract: An efficient carbon–sulfur bond formation reaction has been developed under microwave irradiation. This reaction affords a novel and rapid synthesis of thioacetals and sulfides under mild conditions. This method is particularly noteworthy given its experimental simplicity and high generality, and no transition-metal catalysts were needed under our conditions.

Key words: microwave, sulfide, thiol, nucleophilic substitution.

Résumé : Faisant appel à des irradiations microondes, on a mis au point une méthode efficace pour la formation de liaisons carbone–soufre. Cette réaction fournit une nouvelle méthode rapide de synthèse de thioacétals et de sulfures dans des conditions douces. La méthode est particulièrement remarquable en raison de sa simplicité, de son caractère général et du fait que, dans nos conditions, aucun catalyseur métallique n'est nécessaire.

Mots clés : microonde, sulfure, thiol, substitution nucléophile.

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Introduction

The formation of a C–S bond is an important organic reaction (1). For example, the formation of thioacetals provides an excellent method to protect the carbonyl group (2) and can serve to generate umpoled carbonyls (3). Furthermore, some 1,3-dithiolane compounds exhibit remarkable biological activities, which include anticonvulsant (4), radioprotective (5), hepatoprotective (6), anti-tumor (7), and anti-HIV activities (8). In addition, sulfides and their derivatives are also biologically active compounds (9), as well as attractive building blocks in the synthesis of sulfur-containing functional monomers (10). Consequently, numerous synthetic methods for dithioacetals and sulfides have been developed. Representative examples for the preparation of thioacetals include the condensation of a carbonyl compound with thiols in the presence of various Lewis acid catalysts (2, 11) and the reaction of thiols with diiodomethane, dibromomethane, or dichloromethane under strongly basic conditions (12). Sulfide formation is generally carried out by the condensation of activated alkyl halides with alkali metal thiolates (13) or by the reduction of sulfones or sulfoxides using strong reducing agents such as DIBAL–H or $LiAlH_4$ (14). However, many of these clasical methods are limited by their moderate yields, harsh reaction conditions, and tedious work up. Thus, methods for the introduction of a carbon–sulfur bond with the use of transition metal catalysts have been recently developed (15, 16). Among them, the most promising and straightforward methods for the preparation of dithioacetals and sulfides are Tanaka's rhodium-catalyzed reaction of polychloroalkanes with thiols (15*a*) and Ogawa's palladium-catalyzed hydrothiolation of alkynes with thiols (15*h*). Although these methods successfully yield versatile dithioacetals or sulfides, they require a long reaction time, use of expensive catalysts, and vigorous conditions. In particular, the use of transition metals leads to the generation of waste and has a number of hazards associated with it (17). Accordingly, the development of more efficient methods is still in demand.

In the past few years, the utilization of microwave irradiation in organic synthesis has become increasingly popular within the pharmaceutical and academic arenas (18). By taking advantage of this efficient source of energy, compound libraries and optimization can be assembled in a fraction of the time required by classical thermal methods (19). Microwave-assisted protocols have been widely applied to the formation of a variety of carbon–heteroatom and carbon–carbon bonds (20). To the best of our knowledge, the direct metal-free substitution of thiols to polychloroalkanes using

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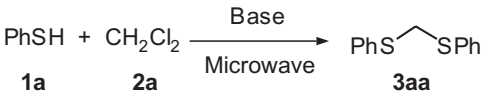
Table 1. Optimization of the reaction conditions.



Entry	Base (equiv.)[a]	Temp. (°C)	Yield (%)[b]
1	K_2CO_3 (1.0)	150	75
2	Cs_2CO_3 (1.0)	150	87
3	DMAP[c] (1.0)	150	72
4	DBU[d] (1.0)	150	89
5	Et_3N (1.0)	150	66
6	DBU (2.0)	150	95
7	DBU (3.0)	150	94
8	DBU (4.0)	150	95
9	DBU (2.0)	60	27
10	DBU (2.0)	90	77
11	DBU (2.0)	120	86

Note: All reactions were conducted using thiophenol **1a** (0.5 mmol) and CH_2Cl_2 (2 mL) in the presence of a base at a certain temperature under microwave irradiation for 20 min.

[a]Based on thiophenol.

[b]Isolated yields based on thiophenol.

[c]4-Methyl aminopyridine.

[d]1,8-Diazabicyclo[5,4,0]undec-7-ene.

high-speed microwave techniques has not been described. Herein, we would like to report our preliminary investigation on the microwave-assisted C–S bond formation reactions, which constitute one of the most efficient and rapid syntheses of dithioacetals and sulfides. Compared with Tanaka's procedure (15*a*), the superiorities of our method include (1) a shorter reaction time and higher yields, (2) a broader substrate scope, and (3) the exclusion of transition-metal catalysts.

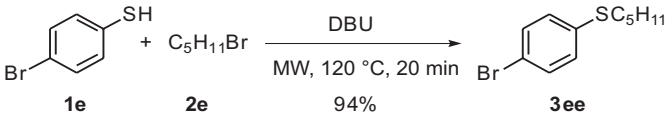
Results and discussion

As a starting point for the development of our microwave-mediated methodology, we chose to study the reaction of thiophenol with dichloromethane for the optimization of reaction conditions, and the results are summarized in Table 1. It was found that the reaction was significantly influenced by the base employed and the temperature (Table 1, entries 1–5 and 9–11). Although both inorganic and organic bases could be used in the reaction, DBU and Cs_2CO_3 are obviously much better than others (Table 1, entries 1–5). Increasing the loading of DBU from 1.0 to 2.0 equiv., based on thiophenol, could dramatically improve the reaction yield (Table 1, entries 4 and 6); however, further increasing the loading of DBU to 4.0 equiv. did not affect the reaction (Table 1, entries 6–8). The reaction temperature is another critical factor for the successful formation of dithioacetals, with the best result being attained at 150 °C (Table 1, entry 6). Decreasing the temperature from this value has been shown to be detrimental to the reaction (Table 1, entries 9–11).

Encouraged by the previous results, we further examined the microwave-assisted reactions of various thiols with polychloroalkanes. From the results shown in Table 2, it can be concluded that both aliphatic and aromatic thiols with an electron-donating or electron-withdrawing group readily undergo this transformation to afford the corresponding dithioacetals or sulfides in good to excellent yiels (Table 2, entries 1–6, 12, and 13). 1,2-Ethanedithiol can also be employed successfully in the reaction (Table 2, entries 7 and 14). In addition to dichloromethane, chloroform, 1,1-dichloropropane, and 1,2-dichloroethane are effective for this microwave-assisted, direct C–S bond formation reaction (Table 2, entries 8–14). 1,3-Dithiolane and 1,4-dithiane can be easily prepared in good isolated yields by the reaction of 1,2-ethanedithiol with dichloromethane and 1,2-dichloroethane, respectively (Table 2, entries 7 and 14).

Next, we investigated the microwave-assisted reaction of *p*-bromothiophenol with pentyl bromide. As expected, the reaction also gave excellent yields and short reaction time in the presence of DBU under microwave irradiation (eq. [1]).

[1]



Conclusions

In conclusion, we established a rapid and efficient method for the synthesis of dithioacetals and sulfides by the direct substitution reaction of thiols with polychloroalkanes without any transition-metal catalyst under microwave irradiation. Particularly, the methodology presented here is attractive because of its shorter reaction time, higher yields, broader substrates scope, and the experimental simplicity. Furthermore, the reaction was developed to meet the increasing demand for green chemistry and environment-friendly chemical processes.

Experimental section

General methods

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Solvents and liquid organic bases were freshly distilled according to the known procedures (21). Column chromatography was performed using 200–300 mesh silica gel. ^{1}H NMR spectra were recorded on Varian Mercury 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ 7.24). Data are reported as follows: chemical

Table 2. Microwave-assisted reactions of thiols with polychloroalkanes.

Entry	Thiol	Polychloro-alkane	Product		Yield (%)[a]
1	PhSH **1a**	CH_2Cl_2 **2a**	PhS, PhS	**3aa**	95
2	*p*-Me-C_6H_4SH **1b**	CH_2Cl_2 **2a**	*p*-Me-C_6H_4S, *p*-Me-C_6H_4S	**3ba**	94
3	*p*-MeO-C_6H_4SH **1c**	CH_2Cl_2 **2a**	*p*-MeO-C_6H_4S, *p*-MeO-C_6H_4S	**3ca**	95
4	*p*-Cl-C_6H_4SH **1d**	CH_2Cl_2 **2a**	*p*-Cl-C_6H_4S, *p*-Cl-C_6H_4S	**3da**	90
5	*p*-Br-C_6H_4SH **1e**	CH_2Cl_2 **2a**	*p*-Br-C_6H_4S, *p*-Br-C_6H_4S	**3ea**	93
6[b]	*n*-C_8H_7SH **1f**	CH_2Cl_2 **2a**	*n*-C_8H_{17}S, *n*-C_8H_{17}S	**3fa**	86
7	HS, SH **1g**	CH_2Cl_2 **2a**	S, S	**3ga**	72
8	PhSH **1a**	Cl, Cl **2b**	SPh, SPh	**3ab**	79
9	PhSH **1a**	Cl, Cl **2c**	Cl, SPh	**3ac**	89
10[b]	PhSH **1a**	Cl, Cl **2c**	PhS, SPh	**3ac'**	91
11	PhSH **1a**	$CHCl_3$ **2d**	PhS, SPh, SPh	**3ad**	72
12	*p*-Br-C_6H_4SH **1e**	Cl, Cl **2b**	SC_6H_4-Br-*p*, SC_6H_4-Br-*p*	**3eb**	95
13	*p*-Br-C_6H_4SH **1e**	Cl, Cl **2c**	Cl, SC_6H_4-Br-*p*	**3ec**	92
14	HS, SH **1g**	Cl, Cl **2c**	S, S	**3gc**	81

Note: For the detailed experimental procedure, see supporting information.[3]
[a]Isolated yields based on thiols.
[b]THF as the solvent.

shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.7). Elemental analysis was performed on a Vario EL III instrument. All experiments were performed in a SmithSynthesizer producing controlled irradiation at 2450 MHz with a power of 0–300 W.

[3] Supplementary data for this article are available on the journal Web site (http://canjcehm.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 5095. For more information on obtaining material, refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml.

Typical procedure for the microwave-assisted reaction of thiol with polychloroalkane

A 5.0 mL process vial was charged with polychloroalkane (2 mL), thiol (0.5 mmol), and DBU (1.0 mmol). The vial was then capped with a Teflon septum and irradiated with microwave to 150 °C for 20 min. After cooling, the reaction mixture was poured into water and extracted with dichloromethane (3 × 5 mL). The combined organic phase was dried over $MgSO_4$ and then filtered. The solvent was evaporated, and the residue was purified by flash chromatography to give the desired dithioacetals or sulfides in good to excellent yields (72%–95%).

Di(phenylthio)methane (3aa) (22)

White solid; mp 30–34 °C; yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43–7.27 (m, 10H), 4.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.1, 130.8, 129.1, 127.2, 40.5.

Di(p-tolylthio)methane (3ba) (23)

White solid; mp 40–42 °C; yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.32 (d, J = 6.4 Hz, 4H), 7.13–7.11 (d, J = 6.8 Hz, 4H), 4.26 (s, 2H) 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 131.5, 131.3, 129.7, 41.9, 21.1.

Di(4-methoxyphenylthio)methane (3ca)

White solid; mp 66–67 °C; yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (dd, J = 2.4, 6.4 Hz, 4H), 6.85 (d, J = 9.2 Hz, 4H), 4.15 (s, 2H), 3.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 134.4, 125.2, 114.6, 55.3, 44.5. Anal. calcd. for $C_{15}H_{16}O_2S_2$: C 61.61, H 5.52; found: C 61.69, H 5.48.

Di(4-chlorophenylthio)methane (3da) (23)

White solid; mp 42–43 °C; yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J = 6.8 Hz, 4H), 7.12 (d, J = 6.8 Hz, 4H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.6, 133.0, 132.4, 129.1, 41.2.

Di(4-bromophenylthio)methane (3ea)

White solid; mp 70.5–72.0 °C; yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.3 (d, J = 8.4 Hz, 4H), 7.26 (d, J = 8.4 Hz, 4H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.6, 132.5, 132.1, 121.5, 40.8. Anal. calcd. for $C_{13}H_{10}Br_2S_2$: C 40.02, H 2.58; found: C 40.21, H 2.61.

Di(octylthio)methane (3fa) (15a)

Colorless oil; yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (t, J = 1.2 Hz, 2H), 2.62 (t, J = 6.8 Hz, 4H), 1.55–1.60 (m, 4H), 1.27–1.38 (m, 20H), 0.88 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.4, 31.8, 30.8, 29.2, 29.2, 28.9, 22.6, 14.0.

1,3-Dithiolane (3ga) (24)

Colorless oil; yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.86 (d, J = 0.4 Hz, 2H), 3.16 (d, J = 0.8Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.0, 34.3.

1,1-Di(phenylthio)propane (3ab)

Pale yellow oil; yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.24 (m, 10H), 4.35 (t, J = 6.4 Hz, 1H), 1.88 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.5, 132.8, 128.7, 59.9, 28.8, 11.5. Anal. calcd. for $C_{15}H_{16}S_2$: C 69.18, H 6.19; found: C 69.04, H 6.32.

1-Chloro-2-phenylthioethane (3ac) (25)

Colorless oil; yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.24 (m, 5H), 3.61 (t, J = 4.2 Hz, 2H), 3.21 (t, J = 4.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.3, 130.5, 129.3, 127.1, 42.1, 35.9.

1,2-Di(phenylthio)ethane (3ac′) (26)

White solid; mp 92–93 °C; yield 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32–7.21 (m, 10H), 3.08 (d, J = 2.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.0, 130.0, 129.0, 126.5, 33.4.

Tris(phenylthio)methane (3ad)

Pale yellow oil; yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49–7.30(m, 15H), 5.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.1, 133.1, 129.1, 128.5, 64.9. Anal. calcd. for $C_{19}H_{16}S_3$: C 67.02, H 4.74; found: C 67.30, H 4.86.

1,1-Di(4-bromophenylthio)propane (3eb)

Colorless oil; yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43–7.28(m, 8H), 4.28 (t, J = 6.6 Hz, 1H), 1.84 (m, 2H), 1.12 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 133.1, 132.0, 122.1, 60.3, 28.8, 11.8. Anal. calcd. for $C_{15}H_{14}Br_2S_2$: C 43.08, H 3.37; found: C 43.29, H 3.30.

1-Chloro-2-(4-bromophenylthio)ethane (3ec)

White solid; mp 134–136 °C; yield 92%. ^{1}HNMR (400 MHz, $CDCl_3$) δ: 7.45–7.23 (m, 4H), 3.60 (m, 2H), 3.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.5, 132.3, 132.0, 121.1, 42.1, 36.2. Anal. calcd. for C_8H_8BrClS: C 38.19, H 3.21; found: C 38.07, H 3.33.

1,4-Dithiane (3gc) (27)

White solid; yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.90 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.1

4-Bromophenylthiopentane (3ee)

Colorless oil; yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.16 (m, 4H), 2.89 (t, J = 7.4 Hz, 2H), 1.67–1.25 (m, 6H), 0.91 (t, J = 5.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.3, 131.8, 130.3, 119.3, 33.6, 30.9, 28.7, 22.2, 13.9. Anal. calcd. for $C_{11}H_{15}BrS$: C 50.97, H 5.83; found: C 51.04, H 5.77.

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