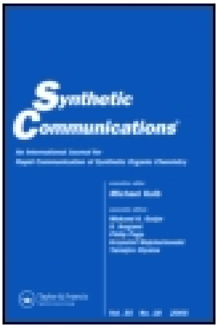

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Jin-Xian Wang [a] , Lin Bai [b] & Zhanxiang Liu [a]
[a] Department of Chemistry, Northwest Normal University, Lanzhou, 730070, P.R.C.
[b] Department of Chemistry, Lanzhou Teachers College, Lanzhou, 730070, P.R.C.

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SYNTHESIS OF SODIUM DISELENIDES AND ITS REACTION WITH BENZOYL CHLORIDE UNDER PHASE TRANSFER CATALYSIS AND MICROWAVE IRRADIATION CONDITIONS

Jin-Xian Wang, [a]* Lin Bai [b] and Zhanxiang Liu [a]

[a] Department of Chemistry, Northwest Normal University, Lanzhou,730070, P. R. C.

[b] Department of Chemistry, Lanzhou Teachers College, Lanzhou,730070, P. R. C.

Abstract A simple, fast and efficient procedure for the synthesis of dibenzoyl diselenides involves the reaction of selenium with sodium hydroxide under phase transfer catalysis and microwave irradiation conditions to give sodium diselenides, which reacts with benzoyl chloride at 0-3 ℃ and conventional conditions to afford the dibenzoyl diselenides. The effect of microwave irradiation power, reaction time, solvent and operational method on the reaction is investigated.

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* To whom the correspondance should be addressed

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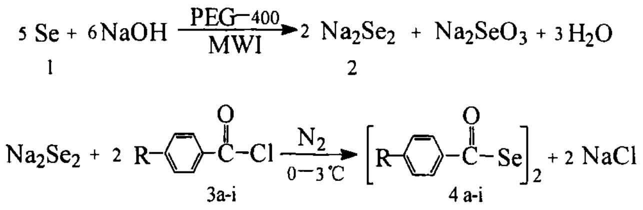
Many methods[1-8] have been described for the preparation of sodium diselenides, which are important for the synthesis of diaryl diselenides. The reaction of selenium with dense alkali under phase transfer catalysis and ultrasound-PTC is a good method for the preparation of sodium diselenides, which reacts with benzoyl chloride to afford the dibenzoyl diselenides[9, 10].

Microwave heating has been used for a wide variety of applications including the rapid synthesis of organic compound and some important reviews have been published.[11] Recently, we have reported the synthesis of the aromatic ethers and chiral substitute glycerol sulfide ethers.[12]

We have now used phase transfer catalysis and microwave irradiation (MWI) method for the preparation of sodium diselenides. Then the reaction of sodium diselenides with benzoyl chloride synthesize the dibenzoyl diselenides. This method is simply and fast and high yield. The reactions are shown in Scheme 1 and the results are summarized in Table 1.



a R = H c R = 4-Cl e R = 4-Br g R = 2-I i R = 3,4-$(OCH_3)_2$
b R = 4-CH_3 d R Ph = PhCH=CH- f R = 2-Br h R = 4-NO_2

Scheme 1

Table 1 Dibenziyl diselenides 4a-i prepared

Entry	Product	Time		M.P.	Lit. M.P.	Yield
		(1)min/w	(2)min/℃	[℃]	[℃][10]	[%]
4a	$(C_6H_5COSe)_2$	12/750	30/0-3	130-131	130-131	90.6
4b	$(p\text{-Me }C_6H_4COSe)_2$	12/750	30/0-3	109-110	109-110	75.4
4c	$(p\text{-Cl }C_6H_4COSe)_2$	12/750	60/0-3	128-129	128-129	81.2
4d	$(C_6H_4CH{=}CHCOSe)_2$	12/750	30/0-3	136-137	136-137	79.7
4e	$(p\text{-Br }C_6H_4COSe)_2$	12/750	60/0-3	150-151	150-151	82.0
4f	$(o\text{-Br }C_6H_4COSe)_2$	12/750	60/0-3	94-95	94-95	78.5
4g	$(o\text{-I }C_6H_4COSe)_2$	12/750	60/0-3	141-142	141-142	75.8
4h	$(p\text{-NO}_2\text{ }C_6H_4COSe)_2$	12/750	60/0-3	160-161	160-161	80.9
4i	$[3,4\text{-}(OCH_3)_2C_6H_3COSe]_2$	12/750	90/0-3	149-150	149-150	83.2

Results and Discussion

Using the reaction of selenium with benzoyl chlorides as an example, we investigated the effect of the power and time of microwave irradiation on the reaction. The results are summarized in Table 2 and Table 3. It was found the high yield of dibenzoyl diselenide can be obtained in 750 W power for 12 min under microwave irradiation conditions.

Table 2 Effect of the power of MWI on the formation of dibenzoyl diselenide

P/ W	375	450	525	600	675	750
Yield/ %	50.8	64.3	73.8	80.1	87.2	90.6

Table 3 Effect of the time of MWI on the formation of dibenzoyl diselenide

Time/ min	4	6	8	10	12
Yield/ %	45.7	58.2	71.6	88.7	90.6

We also studied the effect of different phase-transfer catalysts on the reaction of Se_2^{2-} with benzoyl chloride. It was found that the activities of the catalysts are in the following sequence: PEG-400 > PEG-600 > Bu_4NBr > Bu_4NI. The results show in Table 4.

Table 4 Effect of PTC on the formation of dibenzoyl diselenide

Catalysts	PEG-400	PEG-600	Bu_4NBr	Bu_4NI
Yield/ %	90.6	88.2	72.5	68.4

The quantity of water on the formation of dibenzoyl diselenide was studied using benzene as solvent under phase transfer catalysis. We consider that the quantity of water is very important in the reaction. On the one hand the more water was added, the complete the reaction of Se with NaOH absorbed MWI quickly; On the other hand if the more water was added, the less yield of dibenzoyl diselenide was obtained because of hydrolysis of benzoyl chloride. Experiment results showed that 2 mL water was added into the system, the efficiency was very good.

Compare with other methods for synthesis of dibenzoyl diselenide, the synthesis under microwave irradiation conditions has advantages of rapidity and high yield. Table 5 shows that the results each method were applied in our laboratory.

Table 5 Compare with WMI and other method for Na_2Se_2 of preparation

Experimental	Conditions	Time
WMI-PTC	750 W	12 min
PTC [9]	65-70 ℃	2.5-3 h
Ultrasound-PTC	20-45 ℃	1.5 h

EXPERIMENTAL

IR spectra were measured for KBr discs using an Alpha Centauri FT-IR spectrophotometer. ^{1}HNMR spectra (80 MHz) were recorded in $CDCl_3$ using a FT-80 spectrometer. J Values are given in Hz. Microanalyses were measured using a Carlo Erba 1106 microelemental analyser. Microwave irradiation are carried out with an improved reflux microwave oven using an inert gases protector.[13]

General Procedure: Selenium powder (2.5 mmol) was added to a mixture of PEG-400 (0.1 mmol), sodium hydroxide (30 mmol), benzene (30 mL) and water (2 mL) after which the reaction mixture was irradiated under MWI at 750 W for 12 min. The benzoyl chloride (2.0 mmol) was added and the reaction mixture was stirred under N_2 or Ar at 0-3 ℃ for 30 min. The aqueous layer changed from brown-red to colorless immediately. The organic layer was separated, inorganic layer was washed with benzene and then dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to afford the pure dibenzoyl diselenides. Recrystallization from hexane or benzene gave the analytically pure products.

4a. IR ν (KBr): 3040w, 1738s, 1684s, 864s, 489m. ^{1}H-NMR($CDCl_3$): δ 7.41-8.11(10H, m, 2×ArH). Anal. Calcd for $C_{14}H_{10}O_2Se_2$: C %, 45.65; H%, 2.71. Found: C%, 45.68; H%, 2.74.

4b. IR ν (KBr): 3042w, 1740s, 1700s, 867s, 460m; ^{1}H-NMR($CDCl_3$): δ 7.25-7.96(8H, q, 2×ArH, J=8.10), 2.42(6H,s, 2×CH_3). Anal. Calcd. for $C_{16}H_{14}O_2Se_2$: C %, 48.48; H%, 3.54. Found: C%, 48.65; H%, 3.68.

4c. IR ν (KBr): 3047w, 1734s, 1692s, 869s, 466m; ^{1}H-NMR($CDCl_3$): δ 7.25-8.20(8H, q, 2×ArH, J=8.60). Anal. Calcd. for $C_{16}H_{14}O_2Se_2$: C %, 38.44; H%, 1.83. Found: C%, 38.62; H%, 1.89.

4d. IR ν (KBr): 3065w, 1684s, 1631s, 872m, 481m; ^{1}H-NMR ($CDCl_3$): δ 6.45(2H, s, 2×CH=C-), 6.56(2H, s, 2×CHCO), 7.26-7.91(10H, m, 2×ArH). Anal. Calcd. for $C_{18}H_{14}O_2Se_2$: C %, 51.43; H%, 3.33. Found: C%, 51.68; H%, 3.21.

4e. IR ν (KBr): 3064w, 1724s, 1693s, 866m, 456m; ^{1}H-NMR($CDCl_3$): δ 7.56-8.05(8H, q, 2×ArH, J=8.61). Anal. Calcd. for $C_{14}H_8Br_2O_2Se_2$: C %, 31.94; H%, 1.52. Found: C%, 31.42; H%, 1.41.

4f. IR ν (KBr): 3044w, 1738s, 1698s, 854s, 459m; ^{1}H-NMR($CDCl_3$): δ 7.34-7.85(8H, m, 2×ArH). Anal. Calcd. for $C_{14}H_8Br_2O_2Se_2$: C %, 31.94; H, 1.52. Found: C%, 31.93; H%, 1.48.

4g. IR ν (KBr): 3047w, 1740s, 1692s, 850s, 457m; ^{1}H-NMR($CDCl_3$): δ 7.38-7.90(8H, m, 2×ArH). Anal. Calcd. for $C_{14}H_8I_2O_2Se_2$: C %, 27.09; H%, 1.29. Found: C%, 27.01; H%, 1.27.

4h. IR ν (KBr): 3104w, 1724s, 1697s, 840m, 551m; ^{1}H-NMR($CDCl_3$): δ 7.25-8.46(8H, q, 2×ArH, J=8.46). Anal. Calcd. for $C_{14}H_8N_2O_6Se_2$: C %, 36.68; H%, 1.75; N%, 6.1. Found: C%, 37.02; H%, 1.80; N%, 6.19.

4i. IR ν (KBr): 3020w, 2836m, 750s, 1655m, 866s, 462m; ^{1}H-NMR($CDCl_3$): δ 7.19-7.94(6H, m, ArH); 2.40-2.45(12H, d, 2×OCH_3). Anal. Calcd. for $C_{18}H_{18}O_6Se_2$: C %, 44.26; H%, 3.69. Found: C%, 44.55; H%, 3.85.

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