Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A Convenient One-Pot Synthesis of Dibenzyl Diselenides Under Microwave Irradiation Conditions

Jin-Xian Wang [a] , Lin Bai [b] , Wenbo Li [a] & Yulai Hu [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.

To cite this article: Jin-Xian Wang , Lin Bai , Wenbo Li & Yulai Hu (2000) A Convenient One-Pot Synthesis of Dibenzyl Diselenides Under Microwave Irradiation Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:2, 325-332, DOI: 10.1080/00397910008087325

To link to this article: http://dx.doi.org/10.1080/00397910008087325

SYNTHETIC COMMUNICATIONS, 30(2), 325–332 (2000)

A CONVENIENT ONE-POT SYNTHESIS OF DIBENZYL DISELENIDES UNDER MICROWAVE IRRADIATION CONDITIONS

Jin-Xian Wang [a*], Lin Bai [b], Wenbo Li [a] and Yulai Hu [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, rapid and efficient method for the synthesis of dibenzyl diselenides under microwave irradiation is reported. The effect of microwave irradiation power, times and solvent on the reaction is investigated.

---

* To whom the correspondance should be addressed.

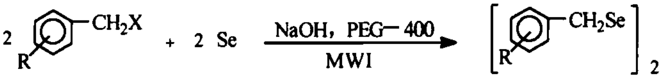
www.dekker.com

Diaryl diselenides are important intermediates in the synthesis of organoselenium compounds. Many methods[1] have been described for the synthesis of diaryl and dialkyl diselenides. The reaction of diselenide anion with appropriate halides is a well known method for the preparation of symmetrical diselenides[2]. The diselenide anion has been prepared by reaction of selenide anion with 1 equiv. of selenium[3], or by reduction of selenium with 1 equiv. of reducing agent. Commonly used reagents for the reduction of selenium are alkali metals in liquid ammonia[4,5], dibenzethine in tetrahydrofuran[6], sodium borohydride in ethanol or water[7], hydrazine hydrate[8], lithium triethylborohydride in THF[9], tetraalkylammonium borohydride in toluene[10] and phenylhydrazine in DMF. Dibenzyl diselenides can be prepared from Grignard reagents[12], sulfonic acid esters[13], electro-chemical reduction[14, 15], ultrasound-induced electro-chemical synthesis[16,17], and by reaction of $(CH_3OMg)_2Se_2$ with halides[18]. All these methods involve use of expensive reagents or solvents, or long reaction times.

Recently, we have reported the synthesis of dibenzyl diselenides and dibenzoyl diselenides from the reaction of selenium with halides in alkaline medium under phase transfer conditions[19,20].

In recent years, interest has been shown in the study of microwave assisted organic synthesis, and some important reviews have been published.[21] However, few practical applications have been devised for the synthesis of organoselenium compounds. Recently, we have also reported the synthesis of the symmetrical and chiral substituted glycerol sulfide (or selenide) ethers.[22]

We have now found that dibenzyl diselenides 3 can be obtained from the reaction of benzyl halides 1 with selenium 2 in a two-phase system consisting of benzene, water. Using polyethylene glycol-400 as the catalyst under microwave irradiation condition. This method is very simple, rapid and affords good yields of dibenzyl diselenides. The reactions are shown in Scheme 1 and the results of the compounds prepared are enlisted in Table 1.



1a-i 2 3a-i

a	R=H,	X=Cl	d	R=4-Br,	X=Br	g	R=2-CH_3,	X=Br
b	R=H,	X=Br	e	R=2-Br,	X=Br	h	R=4-NO_2,	X=Br
c	R=4-Cl,	X=Br	f	R=4-CH_3,	X=Br	i	R-⊙ = β-$C_{10}H_7$,	X=Br

Scheme 1

Results and Discussion

Using the reaction of selenium with benzyl halides 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. The results shown that the high yield compounds 3 can be obtained in 750 W power for 15 min under microwave irradiation conditions.

The efficiency of various solvents on the formation of dibenzyl diselenide was studied using phase-transfer catalysis under MWI in 750 W for 15 min (Molar ratio: $PhCH_2Br$: Se : NaOH : PEG-400 =1:1.25:15:0.05). Benzene was found to be an effective solvent for the reaction. The effects of various solvents in the synthesis of dibenzyl diselenide are shown in Table 4. Although THF was found also to be an effective solvent for the synthesis of dibenzyl diselenide in high yield, the purity of product is more difficult.

The mechanism[19] of inorganic and organic synthesis under phase-transfer catalysis has been discussed. The heating effect utilized in microwave assisted organic transformations is due to the dielectric constant of solvent. The larger the dielectric constant, the greater the

Table 1 Dibenzyl diselenides 3a-i prepared

Entry	Product	Time/Power	M. P. [℃]	Lit. M. P. [℃][19]	Yield [%]
3a	$(C_6H_5CH_2Se)_2$	15min/750W	90-91	90-91	75.0
3b	$(C_6H_5CH_2Se)_2$	15min/750W	90-91	90-91	95.0
3c	$(p\text{-}ClC_6H_4CH_2Se)_2$	15min/750W	77-78	77-78	78.0
3d	$(p\text{-}BrC_6H_4CH_2Se)_2$	15min/750W	99-100	99.5-100.5	84.6
3e	$(o\text{-}BrC_6H_4CH_2Se)_2$	15min/750W	99-100	99-100	82.0
3f	$(p\text{-}MeC_6H_4CH_2Se)_2$	15min/750W	53-54	53-54	91.3
3g	$(o\text{-}MeC_6H_4CH_2Se)_2$	15min/750W	86-87	86-86.5	82.4
3h	$(p\text{-}NO_2C_6H_4CH_2Se)_2$	15min/750W	110-111	110-111	72.4
3i		15min/750W	133-134	133-134	80.2

Table 2 Effect of the power of MWI on the formation of dibenzyl diselenide [a]

Power (W)	375	525	600	675	750
Yield (%) [b]	54.6	71.8	86.4	91.2	95.0

[a] Molar ratio: $PhCH_2Br:Se:NaOH:PEG\text{-}400=1:1.25:15:0.05$. [b] Yield of isolated product.

Table 3 Effect of the time of MWI on the formation of dibenzyl diselenide [a]

Time(min) [a]	8	10	12	14	15	18
Yield(%)	38.6	50.1	71.6	91.0	95.0	82.6

[a] The reaction was monitored by TCL on silica gel.

Table 4 Effect of solvents on the synthesis of dibenzyl diselenide

Solvents	C_6H_6	C_6H_6 - H_2O	THF
Dielectric constant($\varepsilon^{25℃}$)	2.274	2.274-78.54	7.58
MP/ ℃	80.1	80.1-100	67
Yield(%)	0	95.0	95.2

coupling with microwaves[21,22]. We found when power is high (750 W), reaction time is long (15 min) and using H_2O-C_6H_6 which has large dielectric constant as solvent, the one-pot reaction is very good.

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 inext gases protector.[22b]

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), water (5 mL) and $PhCH_2Br$ (2.0 mmol) was added after which the reaction mixture was irradiated under N_2 and MWI at 750 W for 15 min. The aqueous layer changed from brown-red to colorless immediately. The organic layer was separated, inorganic layer was washed with benzene (3 × 15 mL) and then dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to afford the pure dibenzoyl diselenides. Recrystallization from ethanolor benzene gave the analytically pure products.

Dibenzyl diselenide 3a & 3b. IR ν (KBr): 3041w, 970m, 810s, 760m, 490w, 420w. ^{1}H-NMR($CDCl_3$): δ 7.25-7.60 (10H, m, 2×ArH), 3.84(4H, S, 2×CH_2Se). Anal.Calcd for $C_{14}H_{14}Se_2$: C%, 49.42; H%, 4.12%; Found: C%, 49.46; H%, 4.22.

Bis(4-chlobenzyl) diselenide 3c. IR ν (KBr): 3046w, 2914w , 2860w, 821m, 716m, 480m. ^{1}H-NMR($CDCl_3$): δ 7.05-7.33 (8H, q, 2×ArH, J=8.62), 3.82(4H, S, 2×CH_2Se). Anal.Calcd for $C_{14}H_{12}Cl_2Se_2$: C%, 41.07; H%, 2.93%; Found: C%, 40.94; H%, 2.97.

Bis(4-bromobenzyl) diselenide 3d. IR ν (KBr): 3050w, 2942w, 2867w, 819m, 711m, 471m. ^{1}H-NMR(CDCl$_3$): δ 7.00-7.48(8H, q, 2×ArH, J=8.42), 3.80(4H, S, 2×CH$_2$Se). Anal.Calcd for $C_{14}H_{12}Br_2Se_2$: C%, 33.73; H%, 2.41; Found: C%, 33.86; H%, 2.43.

Bis(2-bromobenzyl) diselenide 3e. IR ν (KBr): 3040w, 2940w, 2879w, 826m, 754m, 432m. ^{1}H-NMR(CDCl$_3$): δ 7.04-7.58(8H, m, 2×ArH), 4.01(4H, S, 2×CH$_2$Se). Anal.Calcd for $C_{14}H_{12}Br_2Se_2$: C%, 33.73; H%, 2.41; Found: C%, 33.82; H%, 2.50.

Bis(4-methylbenzyl)diselenide 3f. IR ν (KBr): 3040w, 2916w, 2856w, 821m, 714m, 480m. ^{1}H-NMR(CDCl$_3$): δ 7.11-7.25(8H, d, 2×ArH),3.84(4H, S, 2×CH$_2$Se), 2.32(6H, S, 2×CH$_3$). Anal.Calcd for $C_{16}H_{18}Se_2$: C%, 52.17; H%, 5.00; Found: C%, 51.91; H%, 5.08.

Bis(2-methylbenzyl) diselenide 3g. ν IR (KBr): 3018w, 2930w, 2860w, 764s, 722m, 485m. ^{1}H-NMR(CDCl$_3$): δ 7.12-7.33 (8H, m, 2×ArH),3.89(4H, S, 2×CH$_2$Se), 2.38 (6H, S, 2×CH$_3$). Anal.Calcd for $C_{16}H_{18}Se_2$: C%, 52.17; H%, 5.00; Found: C%, 51.79; H%, 5.21.

Bis(4-nitrobenzyl) diselenide 3h. IR ν (KBr): 3060w, 2946w, 2872w, 864m, 748m, 477m. ^{1}H-NMR(CDCl$_3$): δ 7.16-8.22(8H, q, 2×ArH, J=8.62), 3.91(4H, S, 2×CH$_2$Se). Anal.Calcd for $C_{14}H_{12}N_2 0_4 Se_2$: C%, 39.07;H%, 2.79, N%, 6.51; Found: C%, 39.10; H%, 2.76; N%, 6.46.

Bis(2-naphthylmethyl) diselenide 3i. IR ν (KBr): 3052w, 2940w, 2868w, 821s, 741s, 461m. ^{1}H-NMR δ 7.20-7.81(14H, m, 2×$C_{10}H_7$), 3.93(4H, S, 2×CH$_2$Se). Anal.Calcd for $C_{22}H_{18}Se_2$: C%, 60.00; H%, 4.09; Found: C%, 60.26; H%, 4.22.

References

1 Krief, A.,De Mahieu, A. F., Dumont, W. and Ttabelsi, M., *Synthesis*, **1988**, 131.

2 Sharpless, K. B.and Younh, M.W., *J.Org. Chem.*, **1975**, 40, 947.

3 Degrand, D. P. and Nour,M., *J.Electroanal.Chem.*, **1985**, 53, 213.

4 Bergstorm, F.W., *J.Am. Chem. Soc.*, **1926**, 48, 146.

5 Bogolgubov, G. M., Shlyk, Y. N., *Zh.Obshch. Khim.*, **1969**, 39(10), 1759.

6 Syper, L., Mlochowski, J., *Tetrahedron*, **1988**, 44(19), 6119.

7 Klayman, D. L., Griffin, T. S., *J. Am. Chem. Soc.*, **1973**, 95(1), 197.

8 Syper, L., Mlochowski, J., *Synthesis*, **1984**, (5), 439.

9 Gladysz, J., Homby, J. L., Garbe, J. E., *J. Org. Chem.*, **1978**, 43(6), 1204.

10 Bergman, J., Engman, L., *Synthesis*, **1980**, (7), 569.

11 J. Q. Li, W. L. Bao, P. Lue and X. J. Zhou, *Synth. Commun.*, **1991**, 21, 799.

12 Reich, H, J., Renga, J. M. And Reich, I. L., *J. Am. Chem. Soc.*, **1975**, 97, 5434.

13 Klaymana, D. L. and Gunther, W. H. H.., Organic Selenium Compounds: Their Chemistry Biology, Wiley, New York, **1973**, p. 87.

14 Degrand, C., Nour, M., *J. Electroanal. Chem.*, **1985**, 190, 213.

15 Jeroschewski, P., *J. Prakt. Chem.*, **1982**, 324, 787.

16 Gautheron, B., Tainturier, G., Degrand, C., *J. Am. Chem. Soc.*, **1985**, 107(19), 5579.

17 Degrand, C., Nour, M., *J. Electroanal. Chem.*, **1986**, 199, 211.

18 Gunther, W. I. H. H., *J. Org. Chem.*, **1967**, 32, 3929.

19 Jin-Xian Wang, Wenfeng Cui and Yulai Hu, *J. Chem. Soc. Perkin Trans.* 1, **1994**, (16), 2341-2343.

20 Jin-Xian Wang, Wenfeng Cui, Yulai Hu and Shusheng Zang, *J.Chem. Res., (s)*, **1990**, 230.

21 (a) Galema, S.A.,*Chem. Soc. Rev.*, **1997**, 26, 233-238. (b) Cadidick, S., *Tetrahedron*, **1995**, 51, 10403-10432.

22 (a) Jin-Xian Wang, Yumei Zhang, Danfeng Huang and Yulai Hu, *J.Chem. Res., (s),* **1998**, 216-217. (b)Jin-Xian Wang, Yunsheng Xi, Xiaowei Wu,Yulai Hu, Zhengyin Du, *Synth. Commun., 1998*, 28(24), 4916-4627.

(Received in the USA 29 May 1999)