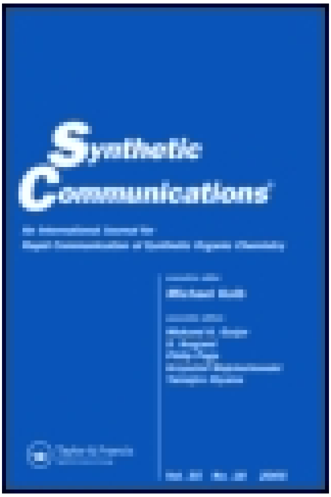

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A Convenient Method for the Preparation of Diaryl Tellurides and Diaryl Selenides

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A CONVENIENT METHOD FOR THE PREPARATION OF DIARYL TELLURIDES AND DIARYL SELENIDES

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ABSTRACT: Sodium hydrogen telluride or selenide reacts rapidly with aryldiazonium fluoborates to give the corresponding symmetric diaryl tellurides or selenides.

Sodium hydrogen telluride has been used for many organic synthetic reactions as a reducing agent or a nucleophile since 1975[1]. Recently we reported a nucleophilic substitution reaction of sodium hydrogen telluride with active aryl halides. The products are corresponding tellurophenols which can be subsequently oxidized to diaryl ditellurides[2].

$$\mathrm{NaHTe + ArX \xrightarrow{DMF} ArTeH \xrightarrow{[O]} ArTeTeAr}$$

In consideration of the electrophilic reactivity of aryldiazonium fluoborate we tried the reaction of it with equimolar sodium hydrogen telluride in dimethylformamide. However, there was obtained not only the expected diaryl ditelluride, but also diaryl telluride

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which was the major product. Obviously, diaryl telluride was formed by the attacking of the strong electrophile, aryl cation Ar^+ on the primary product tellurophenol, before it was oxidized to the corresponding ditelluride. Thus if we increase the mol ratio of the aryldiazonium fluoborate, we shall expect diaryl telluride to be the only product. We then changed the mol ratio of $ArN_2^+BF_4^-$/NaHTe to 2/1, and got only diaryl telluride (see Table 1). The reaction mechanism could be outlined as follows:

$$\underset{1a\text{-}g}{ArN_2^+BF_4^-} \longrightarrow Ar^+ + N_2 + BF_4^-$$

$$Ar^+ + NaHTe \longrightarrow \underset{2a\text{-}g}{ArTeH} + Na^+$$

$$Ar^+ + ArTeH \longrightarrow \underset{3a\text{-}g}{Ar_2Te} + H^+$$

When we used sodium hydrogen selenide instead of sodium hydrogen telluride in the above reaction, diaryl selenide was obtained (see Table 2).

$$NaHSe + 2\underset{1a\text{-}f}{ArN_2^+BF_4^-} \longrightarrow \underset{4a\text{-}f}{Ar_2Se}$$

The reaction listed in Table 1 and 2 ran quickly under mild conditions, the yields were moderate high. Thus a new method of synthesis of symmetric diaryl tellurides and selenides is given. Comparing with methods reported[3-8], it has the advantages of convenient manipulation, short reaction time, easily obtained starting materials and moderate yield.

Table 1. The reaction of sodium hydrogen telluride with two equivalent aryl diazonium fluoborate in DMF

1	Ar	Product[a]	Yield[b] (%)	m.p. (°C) found[c]	m.p. (°C) reported
a	2-$CH_3C_6H_4$	3a	79	37	37-38[9]
b	4-$CH_3C_6H_4$	3b	65	66-67	67[3]
c	4-$CH_3OC_6H_4$	3c	83	52-53	53-54[3]
d	4-ClC_6H_4	3d	70	93.5-94	93-94[8]
e	4-BrC_6H_4	3e	81	119-120	121[10]
f	C_6H_5	3f	54[11]	oil	4[12]
g	2-$C_{10}H_7$	3g	75[11]	120-122	126[13]

a, confirmed by ^1H NMR, IR, MS and Elem. Anal.
b, isolated yield
c, uncorrected

Table 2. The reaction of sodium hydrogen selenide with two equivalent aryl diazonium fluoborate in EtOH

1	Ar	Product[a]	Yield[b] (%)	m.p. (°C) found[c]	m.p. (°C) reported
a	2-$CH_3C_6H_4$	4a	63	61	61-62[9]
b	4-$CH_3C_6H_4$	4b	61	67-68	69-69.5[14]
c	4-$CH_3OC_6H_4$	4c	68	48-49	48[15]
d	4-ClC_6H_4	4d	63	94-95	95-96[16]
e	4-BrC_6H_4	4e	81	112-113	114-115[16]
f	C_6H_5	4f	60[d]	oil	2.5[12]

a b c, same as a b c in Table 1.
d, after purifying with column chromatography.

General procedure for the preparation of diaryl tellurides, exemplified by bis(4-chlorophenyl)telluride(3d):

Tellurium powder (0.64g, 5mmol) and sodium borohydride (0.23g, 6mmol) are placed in a 50 ml three-necked flask. The flask is then evacuated and purged with nitrogen three times. Dimethylformamide (10 ml) is syringed in. The mixture is stirred and heated at 80°C for half an hour and a dark purple solution is then formed. After it is cooled in an ice-water bath, a solution of 4-chlorophenyldiazonium fluoborate (2.48g, 11 mmol) in DMF (4 ml) is slowly injected in by a syringe. The reaction runs quickly with evolving of nitrogen. Then the mixture is stirred for further 15 min. to complete the reaction. After filtration, the filtrate is added with 30 ml of water, extracted with ether(3X20 ml). The combined organic extract is washed with brine (2X20 ml), dried by anhydrous magnesium sulfate, and concentrated to an orange solid, weighs 1.22g, yield 70%. The crude product is recrystalized from ethyl alcohol to give pale orange crystals, m.p. 93.5-94°C, ^{1}H NMR: 7.15(d, 4H), 7.57(d, 4H) ppm; Elem. Anal: Calcd for $C_{12}H_8Cl_2Te$; C, 41.10; H, 2.30. Found: C, 41.63; H, 2.33.

General procedure for the preparation of diaryl selenides, exemplified by bis(2-methylphenyl) selenide(4a):

Selenium powder (0.4g, 5mmol) and sodium borohydride (0.21g, 5.5 mmol) are placed in a 50 ml three-necked flask. The flask is then evacuated and purged with nitrogen three times. Abs. ethyl alcohol (10 ml) is syringed in. The reaction takes place rapidly and selenium powder is then disappeared to give an almost colorless solution. The reactor is cooled in an ice-water bath for several min., a solution of 2-methylphenyldiazonium fluoborate (2.27g, 11 mmol) in DMF (4 ml) is slowly injected in by a syringe. The reaction runs quickly with evolving of nitrogen. Then the mixture is stirred for further 20 min.. After filtration, the filtrate is added with 50 ml of ether, washed with water (3X20 ml). The organic layer is dried with anhydrous sodium sulfate, and concentrated to a solid, weighs 0.82g, yield 63%. The crude product is recrystalized from ethyl alcohol to give red crystals, m.p. 61°C, ^{1}H NMR: 2.37(s, 6H), 7.18(m, 8H) ppm; Elem.Anal.: Calcd for $C_{14}H_{14}Se$: C, 64.37; H, 5.40. Found: C, 64.75; H, 5.61.

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References

1, Suzuki, H.,J.Syn.Org.Chem.Japan,1987,45(6),603.

2, Liu,J.,Qiu,M.,Zhou,X.,Synthetic Commun.,1990,20 (18),2759.

3, Engman,L.,J.Org.Chem.,1983,48,2920.

4, Suzuki,H. and Inouye,M.,Chem.Lett.,1985,389.

5, Irgolic,K.J.,"The Organic Chemistry of Tellurium", Gordon and Breach Science Publishers Inc.,1974,pp105.

6, Zingaro,R.A. and Cooper,C.W.,"Selenium",1974,pp408.

7, Harvey,A.C.,Durig,J.R. and Morrissey,A.C.,J.Chem. Phys.,1969,50,4949.

8, Li,J. and Zhou,X.J.,to be published.

9, Beilsteins H 6,373

10, Irgolic,K.J.,"The Organic Chemistry of Tellurium", Gordon and Breach Science Publishers Inc.,1974,pp112.

11, Zhao,H., BS dissertation of chemistry department of Hangzhou University,1990. We are grateful to Miss Zhao for the preparation of compound 3f and 3g.

12, "Dictionary of Organic Compounds" 5th ed. Chapman and Hall,1982.

13, Lyons,R.E.,Bush,G.C.,J.Am.Chem.Soc.,1908,30,831.

14, Beilsteins H 6,427

15, Beilsteins H 6,871

16, Beilsteins H 6,347

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