

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

# The Reaction of Aryllithium Compounds with Aryl Selenocyanates. A New Synthesis of Unsymmetric Diaryl Selenides<sup>1</sup>

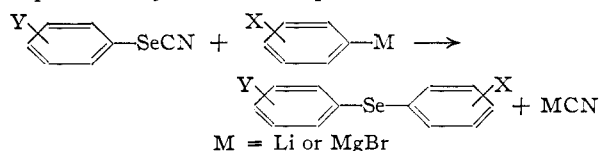
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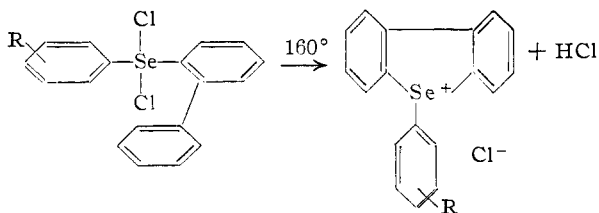
A general synthesis of unsymmetric diaryl selenides, employing the reaction of aryllithium compounds (or aryl Grignard reagents) with aryl selenocyanates, has been developed. Non-oxidizing substituent groups do not seriously affect the reaction. Thirty-nine diaryl selenides, all unsymmetric, were prepared using this reaction. All gave diarylselenium dihalides on subsequent halogenation. The dihalides of the *o*-biphenyl compounds cyclize on heating to form selenonium salts.

A number of procedures appear in the literature for the preparation of unsymmetrical diaryl selenides. These have been recently reviewed.<sup>2</sup> Of these methods, perhaps the best is that of Campbell and McCullough<sup>3</sup> who employed the reactions of diselenides, R<sub>2</sub>Se<sub>2</sub>, with Grignard reagents, R'MgBr, to give the selenide, RSeR', sometimes in excellent yields. However, the necessary diselenides are frequently obtained from the corresponding selenocyanates, RSeCN, by treatment with alkali. This conversion proceeds by an unknown path, and yields of the diselenides are often low.<sup>4,5</sup> Moreover, at best, only half of the selenium of the diselenide may be directly converted to the desired selenide.

The new synthetic method presented here, involving the direct reaction of aryl selenocyanates with aryllithium derivatives, leads directly to diaryl selenides. Grignard reagents may be used in place of aryllithium compounds.



The reaction appears to be quite general, being impaired only by substituents such as the nitro group, which would preferentially react with aryllithium compounds. Purity of reagents affects the reaction but slightly. The major side product is the diselenide Ar<sub>2</sub>Se<sub>2</sub> derived from the selenocyanate; the diselenide is readily removed from the desired selenide by refluxing with alcoholic sodium hydroxide and zinc dust. The presence of cyanide ion in the reaction hydrolysate is indicated by the



(1) A portion of the thesis submitted by Bernard Greenberg in partial fulfillment of the requirements for the B.Sc. degree, Polytechnic Institute of Brooklyn, June, 1956.

(2) (a) E. P. Painter, *Chem. Revs.*, **28**, 174 (1941); (b) T. W. Campbell, H. G. Walker and G. M. Coppinger, *Chem. Revs.*, **50**, 305 (1952).

(3) T. W. Campbell and J. D. McCullough, *THIS JOURNAL*, **67**, 1965 (1945).

(4) F. Challenger, A. T. Peters and J. Halvey, *J. Chem. Soc.*, 1648 (1926).

(5) O. Behagel and H. Seibert, *Ber.*, **65**, 813 (1932).

discharge of the color of ammoniacal copper sulfate solution.

TABLE I  
SELENIDES

X	Y	M.p. (cor.), °C.	B.p. (uncor.) °C.	Mm.	Selenium, %		Yield, %
					Calcd.	Found	
H	<i>o</i> -C <sub>6</sub> H <sub>5</sub>	.....	180-185	1	25.6	25.9	82
H	<i>p</i> -Cl	.....	145-150	1	29.6	30.2	68
H	<i>p</i> -Br	.....	158-161	1	25.3	..	70
H	<i>m</i> -Cl	.....	145-150	1	29.6	29.9	65
H	<i>p</i> -CH <sub>3</sub> O	45-46	120-124	1	30.0	..	86
H	$\beta$ -C <sub>6</sub> H <sub>4</sub>	.....	142-147	1	27.9	28.2	61
<i>p</i> -CH <sub>3</sub>	<i>m</i> -CH <sub>3</sub>	.....	129-134	1	30.2	30.4	75
<i>p</i> -CH <sub>3</sub>	<i>o</i> -C <sub>6</sub> H <sub>5</sub>	79-80	.....	..	24.4	24.5	77
<i>p</i> -CH <sub>3</sub>	<i>p</i> -Cl	72-73	.....	..	28.1	28.4	68
<i>p</i> -CH <sub>3</sub>	<i>m</i> -Cl	.....	160-162	1-2	28.1	27.9	66
<i>p</i> -CH <sub>3</sub>	<i>p</i> -Br	80-81	.....	..	24.2	24.3	75
<i>p</i> -CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub> O	.....	150-153	1	28.5	28.4	88
<i>p</i> -CH <sub>3</sub>	$\beta$ -C <sub>6</sub> H <sub>4</sub>	112-113	.....	..	26.6	26.2	64
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	H	69-70	.....	..	25.6	..	60
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub>	102-103	.....	..	24.4	24.4	66
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>o</i> -C <sub>6</sub> H <sub>5</sub>	98-100	.....	..	20.5	20.1	58
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>p</i> -Cl	117	.....	..	23.0	22.7	59
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>p</i> -Br	126-128	.....	..	20.4	20.5	62
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> O	110-112	.....	..	23.3	23.6	70
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	$\beta$ -C <sub>6</sub> H <sub>4</sub>	120	.....	..	22.0	21.5	57
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>m</i> -Cl	42-44	.....	..	23.0	22.2	56
<i>m</i> -CH <sub>3</sub>	<i>p</i> -Br	64-66	.....	..	24.2	24.4	69
<i>m</i> -CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub> O	.....	147-150	1	28.5	28.7	80
<i>m</i> -CH <sub>3</sub>	<i>p</i> -Cl	.....	150-153	1-2	28.1	28.5	63
<i>m</i> -CH <sub>3</sub>	$\beta$ -C <sub>6</sub> H <sub>4</sub>	45-50	.....	..	26.6	27.6	59
<i>m</i> -CH <sub>3</sub>	<i>o</i> -C <sub>6</sub> H <sub>5</sub>	.....	172-182	1	24.4	24.1	71
<i>m</i> -CH <sub>3</sub>	<i>m</i> -Cl	.....	146-153	1	28.1	28.1	66
<i>m</i> -CH <sub>3</sub>	H	.....	100-102	1	32.0	..	78
<i>p</i> -CH <sub>3</sub>	H	.....	100	1	32.0	..	73
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	<i>m</i> -CH <sub>3</sub>	94-96	.....	..	24.4	23.8	61
<i>p</i> -Br	<i>m</i> -Cl	59-60	.....	..	22.8	22.8	67
<i>p</i> -Br	$\beta$ -C <sub>6</sub> H <sub>4</sub>	118-120	.....	..	21.8	22.1	63
<i>p</i> -Br	<i>o</i> -C <sub>6</sub> H <sub>5</sub>	.....	168-170	<1	20.4	20.1	71
<i>p</i> -Br	<i>p</i> -CH <sub>3</sub> O	69-70	.....	..	23.1	23.0	77
<i>p</i> -Cl	<i>o</i> -C <sub>6</sub> H <sub>5</sub>	.....	156-166	<1	23.0	23.4	69
<i>p</i> -Cl	<i>m</i> -Cl	.....	138-142	<1	26.2	26.6	61
<i>p</i> -Cl	$\beta$ -C <sub>6</sub> H <sub>4</sub>	115-116	.....	..	24.9	25.1	59
<i>p</i> -Cl	<i>p</i> -CH <sub>3</sub> O	.....	145-147	<1	26.6	26.7	76
<i>p</i> -Cl	<i>p</i> -Br	103-104	.....	..	22.8	22.7	72

TABLE II

## UNSYMMETRICAL DIPHENYLSELENIUM DIBROMIDES

Substituents	M.p., °C.	Equiv. wt.	
		Calcd.	Found
<i>p</i> -CH <sub>3</sub> O	125	212.1	211.9
<i>p</i> -CH <sub>3</sub> , <i>p</i> '-Cl	120-122	..	..
<i>p</i> -CH <sub>3</sub> , <i>p</i> '-Br	145-146	242.0	243.4
<i>p</i> -CH <sub>3</sub> , $\beta$ '-C <sub>6</sub> H <sub>4</sub>	114-116	228.5	229.2
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	161-162	..	..
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>p</i> '-CH <sub>3</sub>	146-148	..	..
<i>m</i> -CH <sub>3</sub> , $\beta$ '-C <sub>6</sub> H <sub>4</sub>	108-111	228.5	238.9
<i>p</i> -CH <sub>3</sub>	137-138	..	..
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>m</i> '-CH <sub>3</sub>	149-150	243	255
<i>p</i> -Cl, $\beta$ '-C <sub>6</sub> H <sub>4</sub>	125-127	238.8	237.0

Dichloride and/or dibromide derivatives of the selenides were prepared. The dihalides of the *o*-biphenyl compounds are unstable to heat, readily cyclizing to selenonium salts.<sup>2b</sup>

Here, R may be H-, *p*-CH<sub>3</sub>-, *m*-CH<sub>3</sub>-, *p*-Cl-, *p*-Br- and *p*-C<sub>6</sub>H<sub>5</sub>.

Table I lists the selenides prepared by this method, Table II lists the dichlorides and dibromides derived from these selenides, and Table III lists the selenonium chlorides derived from the *o*-biphenyl selenides.

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### Experimental

The following preparations are typical.

**Phenyl *p*-Tolyl Selenide.**—To 10 cc. of dry ether and 0.36 g. of lithium wire, cut into small pieces, kept under nitrogen, a solution of 4 g. of redistilled bromobenzene in 12 ml. of dry ether was added dropwise with stirring. When the

TABLE III

#### UNSYMMETRICAL DIPHENYLSELENIUM DICHLORIDES

Substituents	M.p., °C.	Equiv. wt.	
		Calcd.	Found
<i>o</i> -C <sub>6</sub> H <sub>5</sub>	Dec. 160	...	...
<i>p</i> -Cl	144-145	158.8	158.1
<i>p</i> -Br	155-156	191.0	190.9
<i>m</i> -Cl	107-109	169.2	167.9
$\beta$ -C <sub>4</sub> H <sub>4</sub>	149-150	177.1	178.6
<i>p</i> -CH <sub>3</sub> , <i>m</i> '-CH <sub>3</sub>	143-144	166.1	167.5
<i>p</i> -CH <sub>3</sub> , <i>o</i> '-C <sub>6</sub> H <sub>5</sub>	Dec. 160	...	...
<i>p</i> -CH <sub>3</sub> , <i>m</i> '-Cl	182-183	176.3	176.0
<i>p</i> -CH <sub>3</sub> , <i>p</i> '-Br	170	198.6	200.0
<i>p</i> -CH <sub>3</sub> , <i>p</i> '-CH <sub>3</sub> O	144-146	174.0	174.3
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	200-201	...	...
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>p</i> '-CH <sub>3</sub>	151-152	197.5	199.5
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>p</i> '-C <sub>6</sub> H <sub>5</sub>	Dec. 160	...	...
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>p</i> '-Cl	170	206.7	208.9
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>p</i> '-Br	171-174	229.5	230.3
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>p</i> '-CH <sub>3</sub> O	166	206.5	205.6
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , $\beta$ '-C <sub>4</sub> H <sub>4</sub>	168-170	214.5	219.1
<i>p</i> -C <sub>6</sub> H <sub>5</sub> , <i>m</i> '-Cl	163-165	206.7	211.0
<i>m</i> -CH <sub>3</sub> , <i>p</i> '-Br	126-127	198.6	199.0
<i>m</i> -CH <sub>3</sub> , <i>p</i> '-CH <sub>3</sub> O	117-118	174.0	173.6
<i>m</i> -CH <sub>3</sub> , <i>p</i> '-Cl	102	176.3	177.1
<i>m</i> -CH <sub>3</sub> , <i>o</i> '-C <sub>6</sub> H <sub>5</sub>	Dec. 160	...	...
<i>m</i> -CH <sub>3</sub> , <i>m</i> '-Cl	117-118	176.3	176.0
<i>m</i> -CH <sub>3</sub>	110-111	...	...
<i>p</i> -CH <sub>3</sub>	126-127	...	...
<i>p</i> -Br, <i>m</i> '-Cl	157-158	208.8	210.0
<i>p</i> -Br, $\beta$ -C <sub>4</sub> H <sub>4</sub>	164-165	216.0	217.8
<i>p</i> -Br, <i>o</i> '-C <sub>6</sub> H <sub>5</sub>	Dec. 160	...	...
<i>p</i> -Br, <i>p</i> '-CH <sub>3</sub> O	146-147	206.5	205.7
<i>p</i> -Cl, <i>o</i> '-C <sub>6</sub> H <sub>5</sub>	Dec. 160	...	...
<i>p</i> -Cl, <i>m</i> '-Cl	152-153	186.4	187.6
<i>p</i> -Cl, <i>p</i> '-CH <sub>3</sub>	151-152	184.3	183.0
<i>p</i> -Cl, <i>p</i> '-Br	193	208.8	209.1

(6) H. Bauer, *Ber.*, **46**, 92 (1913).

metalation appeared to be complete, 5 g. of *p*-tolyl selenocyanate<sup>6</sup> in 12 ml. of ether was added dropwise. The reaction was moderately exothermic. The mixture was allowed to stand for 15 hr., then was hydrolyzed by slow addition of water. The ether layer was separated, dried with anhydrous sodium sulfate and the ether removed. The residue was distilled at 1 mm., yield 4.6 g. (73%), b.p. 100° (1 mm.).

**Phenyl *p*-Biphenyl Selenide.**—To a mixture of 0.25 g. of finely cut lithium wire and 10 cc. of dry ether was added 0.5 g. of *n*-butyl bromide. When the reaction subsided, a solution of 4.9 g. of *p*-bromobiphenyl in 30 ml. of absolute ether was added dropwise as stirring was maintained. Addition was completed in 3 hr., and the mixture was refluxed for an additional hour. A solution of 3 g. of phenyl selenocyanate in 10 ml. of ether was added, and the mixture was allowed to stand under nitrogen overnight, then was hydrolyzed by slow addition of water. The organic layer was separated and dried over anhydrous sodium sulfate. The ether was removed and the residue sublimed at 1 mm. The crude yield was 3.0 g. (60%).

The sublimate was yellow, indicating contamination by a diselenide. Further purification was carried out by treating the product with a mixture of 0.84 g. of zinc dust, 18 ml. of 10% methanolic sodium hydroxide and 1 ml. of benzene. The mixture was kept at 100° for an hour while refluxing was maintained. The mixture was added to 300 cc. of water and the desired selenide extracted with 60 cc. of benzene. The organic layer was filtered, dried over anhydrous sodium sulfate and evaporated to a volume of 15 ml. Boiling methanol was added, and the solution was allowed to cool, yielding white crystals of the selenide, yield 2.64 g. (53%), m.p. 69-70°.

**5-Phenyldibenzselenonium Chloride.**—A solution of 2.5 g. of phenyl *o*-biphenyl selenide in 15 cc. of ether was cooled to 5°. Chlorine gas was passed through the solution until no further precipitation was evident (10 to 15 minutes). The solid was filtered and heated to 170° in a small flask. Frothing occurred, and the material became hard. The solid remaining was dissolved in boiling water, the solution extracted with toluene while hot and the organic layer discarded. The aqueous solution was filtered, using charcoal, and warm concentrated hydrochloric acid was

TABLE IV  
SELENIUM SALTS

R	M.p. (uncor., °C., dec.)	Equiv. wt.		Selenium, %	
		Calcd.	Found	Calcd.	Found
H	252-254	343.5	344.5	23.0	22.7
<i>p</i> -CH <sub>3</sub>	252-254	357.5	356.4	22.1	21.8
<i>m</i> -CH <sub>3</sub>	250-252	357.5	353.0	22.1	22.0
<i>p</i> -Br	252-253	422.5	422.0	18.7	18.6
<i>p</i> -Cl	252-254	378.0	379.3	20.9	20.6
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	252-254	419.5	419.6	18.9	18.9

added. The white crystals which separated on cooling were filtered and dried at 120° for 3 hr., yield 3.0 g. (95%), m.p. 252-254° dec.

**Analysis.**—Selenium analyses were carried out by method of Gould.<sup>7</sup> Titration of the diphenylselenium dihalides was by the method of McCullough, Campbell and Krilanovich.<sup>8</sup> Argentometric equivalent weights of the selenonium chlorides were determined by the method of Swift.<sup>9</sup>

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(7) E. J. Gould, *Anal. Chem.*, **23**, 1502 (1951).

(8) J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Ind. Eng. Chem., Anal. Ed.*, **18**, 638 (1946).

(9) E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1940, p. 397.