

4. Tertiary-butylmagnesium chloride, when added to an excess of acetyl chloride in ether, gives pinacolone in good yields. The yields of the corresponding ketones from higher tertiary Grignard reagents and acetyl chloride are lower.

5. Four homologs of neopentyl alcohol, 2,2-dimethylheptanol-1, 2-methyl-2-ethylpentanol-1, 2-methyl-2-ethylhexanol-1, and 2,2-diethylbutanol-1 have been prepared from the action of formaldehyde with tertiary Grignard reagents.

6. Preliminary studies have been made on the action of carbon dioxide with certain higher tertiary Grignard reagents.

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The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. II¹

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The conversion of simple mercurated organic compounds of the type, $RHgX$, to the mercuri-bis type, R_2Hg , has long been of interest.¹ In the present work this change has been produced in a large number of aromatic mercury compounds by means of sodium alcoholates and alcoholic potassium hydroxide³ and by means of a long known but neglected reagent for this purpose, namely, sodium cyanide.⁴ These studies have been conducted with the chloronaphthylmercuric chlorides prepared from a series of new chloronaphthalene sulfinic acids obtained from the chloronaphthalene sulfonyl chlorides made available in this Laboratory in another research.⁵ The diarylmercury compounds were converted to the arylmercuric bromides and iodides by treatment with mercuric bromide and iodide.

Experimental

A. Mercury Compounds of the Chloronaphthalenes

The Chloronaphthalene Sulfinic Acids.—Of the various ways of converting sulfonyl chlorides to sulfinic acids,⁶ the sodium sulfite method was adopted for the present work. In place of the sodium bicarbonate usually recommended an equivalent amount of dilute sodium hydroxide solution was used. The preparation of 1-chloronaphthalene-6-sulfinic acid may be taken as typical.

A solution of 400 cc. of water, 25.2 g. (0.2 mole) of sodium sulfite, 80 cc. of 20% sodium hydroxide solution (0.4 mole) was heated to boiling in a 1-liter beaker equipped

(1) Whitmore and Sobatzki, *THIS JOURNAL*, **55**, 1128 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore, Hanson and Carnahan, *THIS JOURNAL*, **51**, 894 (1929).

(4) Buckton, *Ann.*, **108**, 105 (1858).

(5) Beattie and Whitmore, *THIS JOURNAL*, **55**, 1546 (1933).

(6) "Organic Syntheses," **2**, 90 (1922).

with a mechanical stirrer. To the stirred solution just below the boiling point was added gradually 52.2 g. (0.2 mole) of finely powdered 1-chloronaphthalene-6-sulfonyl chloride.⁵ The mixture was filtered and the hot filtrate was acidified. After cooling, the sulfinic acid precipitate was filtered off, washed and dried in vacuum over phosphorus pentoxide; yield 44 g., 95%. Six other runs gave an average of 91%. The melting point of the freshly prepared substance was 127–128°. On long standing the melting point gradually rose as high as 250°. The work on the sulfinic acids is summarized in Table I. All of these are new except the 1,5 compound which was reported by Reissert as decomposing above 220°.⁷

TABLE I
CHLORONAPHTHALENE SULFINIC ACIDS

Position of Cl and SO ₂ H	M. p., ^a °C.	Yield, % ^b	G. made	Cl analyses Calcd.: 15.6 Found ^c
1,4	111	91	83	15.4
1,5	121	65	72	15.5
1,6	127–128	91	210	16.1
1,7	128.5–129	77	110	16.0
1,8	105 ^d	97	65	16.0
2,1	87 ^d	88	260	15.5
2,6	°	90	320	15.7
2,7	134	94	220	16.2
2,8	127	82	40	15.4

^a The melting points are of freshly prepared dry samples. In several cases long storage even in tightly stoppered bottles produced increases in m. p. of over 100°. This phenomenon was not studied. ^b Yield based on the pure sulfonyl chloride used. ^c The figures given are the average of at least two analyses in each case. ^d The 1,8 and 2,1 acids darkened rapidly when exposed to light. The latter even decomposed slowly when stored in a dark bottle. All of these sulfinic acids darkened slowly in direct sunlight. ^e Even a freshly prepared sample did not melt at 300°.

The sulfinic acids were soluble in acetone, alcohol, benzene and toluene but sparingly soluble in chloroform and carbon tetrachloride. Cold concentrated sulfuric acid gave a blue or purple color with the following acids, 1,4, 1,5, 2,1 and 2,8, and a green color with the 1,6, 1,7, 1,8, 2,6 and 2,7. A little time was sometimes necessary to develop the green color.

The Chloronaphthylmercuric Chlorides.—These were prepared by the reaction of Peters by boiling the sulfinic acids with aqueous mercuric chloride.⁸ In the preparation of the 1,6 and 1,7 compounds the evolution of sulfur dioxide was very slow while the 1,8 and 2,1 sulfinic acids reacted very rapidly. The nine chloronaphthylmercuric chlorides were insoluble in most solvents except hot xylene, the 1,8 and 2,1 compounds being the most soluble and the 2,6 and 2,7 compounds the least soluble. With the exception of the 2,1 compound they formed white fluffy crystals which usually had a distinct static charge. The 2,1 compound formed fairly large dense plate crystals of a yellowish-white.

The Mercuri-bis-chloronaphthalenes.—These were prepared from the —HgCl compounds by treatment with an excess of alcoholic sodium iodide.

They were also prepared by the new method using an excess of alcoholic sodium cyanide. In each case the nature of the diarylmercury compound was proved by its reaction with mercuric chloride in acetone to give the original chloronaphthylmercuric chloride. In a similar way the new chloronaphthylmercuric bromides and iodides were prepared.

(7) Reissert, *Ber.*, **55**, 873 (1922).

(8) Peters, "Organic Syntheses," **3**, 99 (1923); *Ber.*, **38**, 2567 (1905).

TABLE II
MERCURY COMPOUNDS OF THE CHLORONAPHTHALENES

Position Cl and Hg	ArHgCl				Ar ₂ Hg				ArHgBr				ArHgI			
	M. p., °C.	Yield, ^a %	Analysis Hg calcd.: 50.5 Cl calcd.: 17.8 Found	Cl ^c	M. p., °C.	Yield, ^d %	Analysis Hg calcd.: 38.3 Cl calcd.: 13.5 Found	Cl ^c	M. p., °C.	Yield, ^e %	Analysis Hg calcd.: 45.4 Cl + Br calcd.: 26.1 Found:	Hg ^b Cl + Br ^c	M. p., °C.	Yield, ^e %	Analysis Hg calcd.: 41.0 Cl + I calcd.: 33.2 Found:	Hg ^b Cl + I ^c
1,4	252	69	50.7	18.2	275.5	78	38.4	13.3	251	86	45.6	26.5	233	84	41.3	33.8
1,5	244	83	50.3	18.1	223.5	84	38.5	13.8	231.5	96	45.4	26.4	221.5	87	41.1	33.0
1,6	307	48	50.9	17.6	246	74	38.4	13.7	316	83	45.7	25.6	276.5	82	41.3	33.1
1,7	223	50	50.7	18.1	230.5	95	38.3	13.2	247	81	45.8	26.6	257	76	41.3	33.7
1,8	214	84	50.6	18.3	215.5-216.5	80	38.4	13.7	195.5	89	45.8	26.0	156.5-157.5	86	41.5	32.9
2,1	215	91	50.6	18.3	293.5	40	38.2	13.3	204	74	45.9	26.4	^h			
2,6	260	42	50.3	18.2	260 ^f	77	37.8	13.0	260	81	45.3	25.9	298	82	41.2	32.9
2,7	295	56	51.0	18.1	299	84	38.0	13.7	288	76	45.6	25.9	272	74	41.3	32.8
2,8	232.5	83	50.9	17.5	272.5	83	38.3	13.4	226	69	45.5	26.3	192.5	76	41.5	32.7

^a Yield based on the sulfinic acid used. ^b The mercury analyses were made by iodimetry by the method developed by Ehrenfeld and Sobatzki [Whitmore and Sobatzki, THIS JOURNAL, 55 1128 (1933)]. The figures recorded are the average of two analyses. ^c Average of two analyses. ^d Yield based on the chloromercuri compound using the sodium iodide method. The sodium cyanide method gave slightly lower yields. ^e Yield based on the mercuri-bis compound used. ^f This was the most insoluble of the mercuri-bis compounds. ^g The chloromercuri compounds prepared from the sulfinic acids were checked with those prepared from the mercuri-bis compounds and mercuric chloride. In a few instances the latter process gave slightly purer substances. Mixed m. p. determinations were made in all cases. ^h The 2,1 compound was not made because of lack of material at the end of the research.

In several cases the melting points of the mercuri-bis and chloromercuri compounds were nearly the same. In such cases mixed melting points were used to detect the difference in the compounds. In six out of the nine cases the melting point of the mercuri-bis compound was distinctly higher than that of the corresponding chloromercuri compound. The mercuri-bis compounds formed white minute needles except the 1-mercuri-bis-2-chloronaphthalene and 8-mercuri-bis-1-chloronaphthalene which formed dense white powders.

The Bromomercuri and Iodomercuri Compounds.—Most of the bromomercuri compounds crystallized from the acetone reaction mixture. The 1,6, 2,6 and 2,7 compounds were insoluble in hot acetone and were crystallized from hot xylene as fine white powders. The 1,4 compound crystallized from hot acetone in small golden plates and the 1,2 compound in very dense yellow plates. The others formed white fluffy needle crystals.

The iodomercuri compounds have properties similar to the bromo compounds. The 1,6, 1,7, 2,6 and 2,7 compounds had to be crystallized from hot xylene because of their insolubility in acetone. The 2,7 compound was obtained in small nacreous plates and the 2,8 compound as golden plates. The others formed fine white needles.

The work on the new mercury compounds is summarized in Table II.

B. The Formation of Mercuri-bis Compounds by Alkali Cyanides

Phenyl Compounds.—Phenylmercuric chloride, m. p. 251°, was prepared from aniline in 23% yields by the method of Nesmejanow.⁹ Phenylmercuric acetate, m. p. 145–146°, was prepared by the mercuration of benzene with mercuric acetate in alcohol solution.¹⁰

A solution of 1.3 g. (2 mols) of potassium cyanide in 100 cc. of 95% alcohol was refluxed with 3.12 g. (1 mol) of phenylmercuric chloride for one hour. On cooling 1.37 g. of pure diphenylmercury, m. p. 123–123.5°, separated, a yield of 38%. This reaction is in sharp contrast to the failure of a similar experiment with sodium iodide to give mercury diphenyl.¹ Similar results were obtained with phenylmercuric acetate and 2 or 3 mols of potassium or sodium cyanide. The use of only 1 mol of the cyanide gave phenylmercuric cyanide, m. p. 204–205°, in 85% yield. The same result was obtained with phenylmercuric acetate.

***p*-Tolyl Compounds.**—Di-*p*-tolylmercury, m. p. 243–244°, was obtained in 73% yield by the action of an alcoholic solution of 3 mols of sodium cyanide on *p*-tolylmercuric chloride.

Naphthyl Compounds.— α -Naphthylmercuric chloride, m. p. 189–190°, was obtained in 20% yield from α -naphthylamine.⁹ The β -compound, m. p. 267°, was made in 80% yield from sodium naphthalene-2-sulfinate (Peters) and in 47% yield from β -naphthylamine (Nesmejanow).

TABLE III
PREPARATION OF DI- β -NAPHTHYLMERCURY

Reagents	Solvent	Conditions	M. p. of product, °C.	Yield, %
ArHgCl + 2 mols NaI ^a	Alcohol	Boil, 15 hrs.	238–239	86
ArHgCl + Cu ^b	Pyridine	Boil, 1 hr.	244	70
ArN ₂ Cl.HgCl ₂ + Cu	Acetone	Cold, 1 hr.	241–242	40
ArHgCl + 3 mols NaCN	Alcohol	Boil, 0.5 hr.	247–248	83.5
ArHgCN + 2 mols NaCN	Alcohol	Boil, 0.5 hr.	246–248	

^a Cf. Steinkopf's results with the α -compound, *Ann.*, **413**, 329 (1917). ^b Hein and Wagler, *Ber.*, **58**, 1499 (1925).

(9) Nesmejanow, *Ber.*, **62**, 1010 (1929).

(10) Sneed and Maynard, *THIS JOURNAL*, **44**, 2942 (1922).

Di- β -naphthylmercury was made in a variety of ways. The best method was that using sodium cyanide. The results are summarized in Table III.

The β -naphthylmercuric cyanide used in the last experiment melted at 213–214° and was made by the action of 1 mol of cyanide with the naphthylmercuric chloride.

The di- β -naphthylmercury reacted with mercuric bromide and iodide in boiling acetone to give nearly quantitative yields of β -naphthylmercuric bromide, m. p. 266–266.5° and of β -naphthylmercuric iodide, m. p. 251–251.5°.

Chloronaphthyl Compounds.—Each of the nine chloronaphthylmercuric chlorides was converted to the corresponding mercuri-bis compounds by treatment with 3 mols of sodium cyanide in boiling alcohol. In several cases products with melting points higher than those obtained by the sodium iodide method resulted. The yields, however, were usually slightly lower by the cyanide method.

C. The Formation of Mercuri-bis Compounds by Alcoholates and Alcoholic Alkalies

The arylmercuric chlorides were refluxed with an excess of the alcoholic reagent. The results appear in Table IV. The method is general but is inferior to the older methods.

TABLE IV

ArHgCl	Reagent	Solvent	Time of refluxing	M. p. Ar ₂ Hg, °C.	Yield, %
Phenyl	CH ₃ ONa	Abs. CH ₃ OH	3 hrs.	123.5	34
<i>p</i> -Tolyl	C ₂ H ₅ ONa	Abs. C ₂ H ₅ OH	3 hrs.	244	59
<i>p</i> -Tolyl	C ₂ H ₅ ONa	95% C ₂ H ₅ OH	3 hrs.	244	41
<i>p</i> -Tolyl	(CH ₃) ₂ CHONa	(CH ₃) ₂ CHOH	3 hrs.	244	45
β -Naphthyl	C ₂ H ₅ ONa ^a	Abs. C ₂ H ₅ OH	^a	242–244	57 to 77 ^a
β -Naphthyl	C ₂ H ₅ ONa	95% C ₂ H ₅ OH	^b	241–246	48–62 ^b
β -Naphthyl	CH ₃ ONa	Abs. CH ₃ OH	3.5 hrs.	244	50
β -Naphthyl	(CH ₃) ₂ CHONa	(CH ₃) ₂ CHOH	3.5 hrs.	247	42
β -Naphthyl	KOH ^c	Abs. C ₂ H ₅ OH	3–7 hrs.	245	48–62

^a A series of nine experiments with varying amounts of alcoholate and varying conditions was tried. Less than 2 mols of alcoholate gave impure products. Larger amounts gave no increase in the yields. Refluxing or stirring at room temperature for seven hours gave about the same yield. The method is not as good as the iodide or cyanide method. ^b A series of four experiments. ^c A series of five experiments. Less than 3 mols of potassium hydroxide was ineffective and more gave no increase in yield.

Summary

1. Eight chloronaphthalene sulfinic acids have been prepared for the first time and new data have been obtained for the 1,5 compound.
2. Thirty-five new organic mercury compounds related to the chloronaphthalenes have been prepared. Di- β -naphthylmercury has been obtained with m. p. 247–248°.
3. Equivalent quantities of alkali cyanides convert arylmercuric chlorides to the arylmercuric cyanides but an excess of alkali cyanide gives the diarylmercury compounds. The products are purer but the yields are somewhat lower than with the iodide method for preparing these substances.
4. Sodium alcoholates and alcoholic potassium hydroxide also form the diarylmercury compounds but in yields distinctly lower than those of the iodide and cyanide methods.