phenoneoxime was converted to the amine with sodium amalgam. The amine was changed to its hydrochloride by dissolving in ether and passing in hydrogen chloride; yield, 4.3 g. of the crude salt. A small amount of impurity of inorganic material was separated by dissolving the amine salt in ethanol and filtering. The amine hydrochloride (2.48 g.) was obtained by adding ether to the ethanol solution, as a white compound, decomposing about 290°.

A solution of 2.48 g. of the amine hydrochloride in 25 cc. of water was mixed with 3.62 g. of the ammonium salt of *d*-bromocamphorsulfonic acid dissolved in 20 cc. of water. An immediate precipitate of 5.58 g. of salt occurred which was obviously contaminated with a little ammonium bromocamphor sulfonate. After crystallization from about 100 cc. of water, 4.71 g. was obtained. When pure it melted at 237–239° with decomposition. By subsequent crystallizations, no change in rotation was observed. Rotation: 0.482 g. made up to 15 cc. in 95% ethanol in a 2-dm. tube gave α^{30} +3.99°, $[\alpha]^{30}D$ +62.1°.

The *d*-bromocamphor sulfonate of ordinary diphenylaminomethane has not been described previously. It was prepared in a similar manner as white needles from alcohol, m. p. 236–238° with decomposition.

Anal. Calcd. for $C_{23}H_{28}O_4NBr$: C, 55.8; H, 5.7; neut. equiv., 494. Found: C, 56.0; H, 5.9; neut. equiv., 487. Rotation: 0.505 g. made up to 15 cc. in 95% ethanol gave in a 1-dm. tube, α^{30} + 2.09°, $[\alpha]^{30}D$ +62.1°.

Decomposition of the Bromocamphorsulfonate of the "Heavy" Amine.—The bromocamphorsulfonate (1.5 g.) was decomposed by dissolving in 50 cc. of dilute alkali, extracting with ether, and washing with dilute sodium hydroxide. The amine hydrochloride was precipitated from the ether by hydrogen chloride and reprecipitated from ethanol with ether; m. p. 286–288° with decomposition. Rotation: 0.20 g. made up to 10 cc. in 95% ethanol in a 1-dm. tube gave α 0.00 ± .01.

Summary

1. Phenyl-d_5-phenylaminomethane was prepared according to the method of Clemo from hexadeuterobenzene of 92.5% purity.

2. This product was converted to the *d*-tartrate and *d*-bromocamphorsulfonate salts.

3. By decomposition of the salts only optically inactive amine was obtained. Uncertainty is thus introduced concerning the resolution of substances of the general type $RR'CX_HX_D$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Mercury Derivatives of the *o*-Chlorobenzyl Radical

BY FRANK E. WARE WITH R. M. HIXON

In continuing the studies on the electron-sharing ability of organic radicals,[1] the *o*-chlorobenzylmercuric nitrate, the iodide, and the di-*o*-chlorobenzylmercury were desired. Since none of the mercury derivatives of this radical had been reported, the chloride, bromide, acetate, and the benzoate were also prepared.

The bromide and chloride derivatives were prepared by the reaction of the Grignard derivative of the *o*-chlorobenzyl radical with the corresponding mercuric halides. A 75–76% yield of Grignard reagent, as determined by titration,[2] was prepared from 0.1 mole of *o*-chlorobenzyl chloride. To this was added in small amounts 0.185 mole of the dry powdered mercuric halides. The mixture was refluxed and stirred for several hours, the ether was evaporated off, and the crude material washed several times with 250-cc. portions of a 1% acetic acid solution. The crude compounds were extracted and recrystallized from alcohol or benzene. These two derivatives as well as the iodide were also prepared in almost pure state in quantitative yields by boiling equal molecular quantities of di-*o*-chlorobenzylmercury and the corresponding mercuric halide in ethyl alcohol. The iodide crystals turned yellow when exposed to light for a few minutes. The acetate was prepared in a similar manner.

Di-*o*-chlorobenzyl mercury was obtained by treating an excess of the Grignard reagent with dry mercuric chloride. The halide was added in small portions and the mixture was refluxed and stirred for three hours. After the excess Grignard reagent had been hydrolyzed, the ether layer was evaporated, leaving the impure di-*o*-chlorobenzyl mercury, which was recrystallized from alcohol.

The *o*-chlorobenzylmercuric acetate and the benzoate derivatives were obtained by refluxing *o*-chlorobenzylmercuric chloride with slightly more than the theoretical quantity of the corresponding silver salt in alcohol until the clear solutions gave

(1) Johns with Hixon, THIS JOURNAL, **49**, 1786 (1927); *J. Phys. Chem.*, **34**, 2226 (1930).

(2) Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

SALTS OF *o*-CHLOROBENZYLMERCURY

Salt	Crystal habit, (White)	M. p., °C.	Formula	Percentage, mercury[c] Calcd.	Found	
Di-*o*-chlorobenzylmercury	Need.	101	$C_{14}H_{12}Cl_2Hg$	44.42	44.23	44.51
Iodide	Need.	148	C_7H_6ClHgI	28.01[a]	27.92[a]	27.78[a]
Chloride	Cub.	111	$C_7H_6Cl_2Hg$	55.47	55.48	55.27
Bromide	Cub.	128	$C_7H_6ClHgBr$	49.41	49.29	49.55
Acetate	Need.	101.5	$C_7H_6ClHgO_2C_2H_5$	52.03	52.35	52.21
Benzoate	Need.	58–59[b]	$C_7H_6ClHgO_2C_6H_5$	44.86	45.11	45.16
Nitrate	Trans. plates	96	$C_7H_6ClHgNO_3$	52.23	52.08	52.39

[a] Per cent. iodine. The per cent. mercury in the parent compound, RHgR, and RHgI are very nearly the same—44.42 and 44.27. The iodine was determined by dissolving the salt in the minimum quantity of hot alcohol, precipitating the iodide with alcoholic silver nitrate and weighing the silver iodide. [b] Melting point indefinite. Softened at 56°. [c] The percentage of mercury was determined by the method described by Johns, Peterson and Hixon, THIS JOURNAL, **52**, 2820 (1930).

no test for chloride with alcoholic silver nitrate. The silver chloride was filtered off. The acetate derivative was crystallized by adding warm water to the alcoholic solution and then recrystallized from hot water. The yield was almost quantitative. The benzoate alcoholic solution was concentrated to one-half its volume, and a small amount of brown precipitate (Ag_2O?) was filtered off. When the solution was concentrated to a small volume and cooled, a dark, heavy liquid separated which crystallized in time with difficulty. For the purpose of recrystallization, it was placed in petroleum ether (80 cc. for 0.01 mole of material) and sufficient carbon tetrachloride was added to dissolve it when hot. The nitrate derivative was prepared by dissolving the chloride derivative in the minimum volume of hot absolute alcohol to which was added, with stirring, the theoretical quantity of silver nitrate in hot alcoholic solution. The solution and precipitate were heated on a water-bath at 55 to 60°. Any traces of chlorides were removed by dropping in alcoholic silver nitrate after the mixture had been heated a few hours. After filtering through an asbestos filter, the filtrate was evaporated in an electrically heated vacuum desiccator to a small volume. The transparent plate-like crystals were further purified by recrystallization from ether. They were not affected by diffused sunlight and did not blister the skin as reported for many of the other nitrate derivatives.

In general these compounds are slightly soluble in ether and petroleum ether, and fairly soluble in alcohol, benzene, chloroform, and carbon tetrachloride. Alcohol and benzene are good solvents for recrystallization purposes.

Summary

The chloride, bromide, iodide, acetate, and benzoate of the *o*-chlorobenzylmercury radical and di-*o*-chlorobenzylmercury are reported.

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