fied to give a mercury-containing acid which melted between 250–260°, had a neutralization equivalent of 190, and was completely soluble in sodium bicarbonate solution. The small quantity of product was undoubtedly admixed with some of the coupling product and some of the mercury-acid formed by a mono- X–M interconversion reaction.

Summary

A series of metal–metal interconversion reactions has been carried out between organometallic compounds of lead, tin and mercury and RLi compounds in different media.

The cleavage series of radicals does not agree with the series based on the hydrogen chloride cleavage of unsymmetrical RM compounds, and also varies somewhat with the kind of central metallic atom. Tetraphenyltin is cleaved more rapidly by *n*-butyllithium than is tetraphenyllead. Generalizations have been formulated on the relative effectiveness of some RLi compounds in metal–metal interconversions.

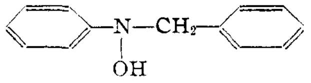
AMES, IOWA RECEIVED JUNE 19, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

N-Benzylphenylhydroxylamine

BY WILLIAM S. EMERSON AND C. H. SHUNK

The alkylarylhydroxylamines constitute a group of compounds whose reactions have received very little study. Since Vavon and Crajcinovic[1] had shown that benzylphenylhydroxylamine (I) could be prepared readily by the partial reduction of a mixture of nitrobenzene and benzaldehyde, we selected this representative as the most convenient member of the series to study.


I

Benzylphenylhydroxylamine is basic, forming readily crystallizable salts. The hydroxyl group is easily benzoylated. When the compound is treated with bromine in carbon tetrachloride, a bromine atom is introduced para to the hydroxylamino group. This was shown by reducing the benzyl-*p*-bromophenylhydroxylamine so obtained to benzyl-*p*-bromoaniline.

The reaction with sulfuric acid was of especial interest since both the hydroxyl group in phenylhydroxylamines and the alkyl group in alkylanilines are known to migrate to the para position. However, in this case the acid first dealkylated the hydroxylamine. When 20% acid was used, derivatives of phenylhydroxylamine were isolated. With more dilute acid (5%) rearrangement occurred, so that *p*-aminophenol was obtained as the product of the reaction.

Experimental

N-Benzylphenylhydroxylamine was prepared by the method of Vavon and Crajcinovic.[1]

The hydrochloride, prepared by passing hydrogen chloride through an ether solution of the hydroxylamine, was crystallized from a mixture of alcohol and ether, m. p. 104–105°.

Anal. Calcd. for $C_{13}H_{14}ONCl$: Cl, 15.1. Found: Cl, 15.1.

The hydrobromide, prepared by the same method, was crystallized from absolute alcohol and ether, m. p. 96–97°.

Anal. Calcd. for $C_{13}H_{14}ONBr$: N, 5.00. Found: N, 4.94.

The benzoyl derivative also was prepared. It crystallized from aqueous alcohol, m. p. 115–117°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: N, 4.62. Found: N, 4.55, 4.70.

N-Benzyl-*p*-bromophenylhydroxylamine.—To a solution of 5 g. of benzylphenylhydroxylamine in 100 cc. of carbon tetrachloride was added a solution of 4 g. of bromine in 40 cc. of carbon tetrachloride. The dark red oil, which first precipitated, slowly crystallized when cooled. It was filtered and recrystallized from aqueous alcohol, m. p. 164–165°, yield 4 g. (56%).

Anal. Calcd. for $C_{13}H_{12}ONBr$: N, 5.04. Found: N, 5.19.

N-Benzyl-*p*-bromoaniline was prepared by reducing the benzyl-*p*-bromophenylhydroxylamine with low pressure hydrogen in the presence of platinum. It melted at 53–54° (55°),[2] after one crystallization from alcohol.

Phenylhydroxylamine.—When 3 g. of benzylphenylhydroxylamine was added to 10 cc. of concentrated sulfuric acid and 40 g. of ice and the resulting mixture boiled for fifteen minutes, a white crystalline solid separated on cooling. This solid, which decomposed at 221–223° and was insoluble in hot alcohol, weighed 2.8 g. When it was treated with benzoyl chloride, N-benzoylphenylhydroxylamine was obtained, m. p. 123–124° (123–124°).[3] Likewise treatment with acetic anhydride yielded N-acetylphenylhydroxylamine, m. p. 67–68° (67.0–67.5°).[4]

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[1] Vavon and Crajcinovic, *Compt. rend.*, **187**, 420 (1928).

[2] Dains and Eberly, THIS JOURNAL, **55**, 3859 (1933).

[3] Ciamician and Silber, *Gazz. chim. ital.*, **36**, II, 172 (1906).

[4] Bamberger and Destraz, *Ber.*, **35**, 1874 (1902).

p-Aminophenol.—After 5 g. of benzylphenylhydroxylamine had been added to 200 cc. of 5% aqueous sulfuric acid, the mixture was heated until solution was complete. After cooling, the mixture was made basic with sodium carbonate. The green oil which separated was removed by extraction with ether and the ether was dried with sodium sulfate and then distilled. The residue was crystallized from an alcohol–ether mixture giving 1 g. (36%) of p-aminophenol, m. p. 183–184° (184°). A mixed melting point with an authentic sample showed no depression.

Summary

Several reactions of N-benzylphenylhydroxylamine have been examined. Sulfuric acid cleaves the molecule giving first phenylhydroxylamine and then rearranging the latter to p-aminophenol.

URBANA, ILLINOIS RECEIVED JULY 10, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Chemistry of the Rye Germ. VI. Allantoin and Other Acetone-Extractives[1]

BY AARON J. IHDE AND H. A. SCHUETTE

Several years ago in this Laboratory it was observed that the oil which had been extracted from rye germs with acetone soon deposited a small amount of crystalline material upon standing. This is apparently a characteristic of a rye oil so recovered, for a similar behavior was never noted in the oil extracted from the same mother substance with any of the other common fat solvents. Further investigations revealed that the crystalline material could be removed in fairly pure form by hot acetone extraction of the germs previously defatted with petroleum ether. A positive Molisch test, together with a sweet taste, indicated a sugar. Recently, upon resumption of this study, it was observed that, when this material was dissolved in hot water, a turbid solution, from which tasteless crystals separated on cooling, resulted. The turbidity was shown to be due to phospholipids. The tasteless, insoluble crystals proved to be allantoin; the sugar was found to be sucrose.

Experimental

Rye germs, which had been made substantially fat-free by extraction with benzene, were exhausted with hot acetone in a Soxhlet-type extractor which was so designed that the rising vapors kept the germs and surrounding solvent near the boiling point of acetone. A 72-hour treatment removed approximately 1% of material which deposited as a light brown, crystalline sediment in the heating flask. Longer extraction failed to remove significantly larger amounts.

Identification of Phospholipids.—Sufficient fat-free rye germ was treated with acetone to obtain 500 g. of solvent-free extract. This extract was refluxed with three 500-ml. portions of ethyl ether. The ether-insoluble portion was transferred to a Büchner funnel and washed with ether until the washings were colorless. The ether solutions and washings were combined and concentrated to approximately one-fourth their original volume to give a brownish, slightly opalescent solution. On addition of four volumes of acetone a white precipitate settled out. On removal of the clear supernatant liquid a gummy white solid remained which quickly turned brown on exposure to air. It was partially, but not entirely, soluble in 95% ethanol and was precipitated by ethanolic cadmium chloride solution. Tests for phosphorus, nitrogen and glycerol were positive. Saponification with ethanolic potassium hydroxide solution yielded typical fatty acids with a neutralization equivalent of 293.1. The Rosenheim bismuth test for choline was positive.

Identification of Allantoin.—The phospholipid-free portion of the extract, amounting to 290 g., was dissolved in 500 ml. of hot water. On cooling, several grams of prism-like crystals separated from solution. The supernatant liquid was removed and concentrated to approximately two-thirds of its original volume and set aside overnight. A second crystal crop was thus obtained. This concentration–crystallization process was twice repeated. The last concentration gave only a few small crystals and a sirupy mother liquor. The total crystal yield was 14.2 g., equivalent to 0.03% of the original rye germ.

The crystals were fairly soluble in hot water but very insoluble in cold water. After several recrystallizations from water the compound melted with decomposition at 231°, though browning began at 220°. Nitrogen was present. Solubility behavior and classification reactions indicated an amide, but it was not possible to hydrolyze it and to isolate a parent acid. Because the compound gave a negative murexide test, it was not a purine. A determination of its nitrogen content indicated that the compound might be allantoin. This was confirmed when the behavior toward Fehling solution and Nessler reagent was typical; when the Schiff furfural test for allantoin was positive; and when a mixed melting point determination with pure allantoin showed no depression. The optical inactivity was also characteristic of allantoin.

Anal. Calcd. for $C_4H_6O_3N_4$: C, 30.39; H, 3.81; N, 35.44. Found: C, 30.44, 30.21; H, 3.81, 3.71; N, 35.31, 35.40.

Identification of Sucrose.—The sirupy mother liquor from which the allantoin had been removed was further

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[1] For communications I, II and V in this series, see THIS JOURNAL, **54**, 3298 (1932), **56**, 210 (1934), and **61**, 1901 (1939); for III, see *Oil and Soap*, **14**, 295 (1937), and for IV see *Cereal Chem.*, **15**, 445 (1938).