tilled and crystallized from alcohol. The hydrocarbon (m. p. 147–148°),[23] recovered in 75% yield, gave no test for sulfur by the second method and could be hydrogenated rapidly.

In experiments conducted with 5 g. of purified pyrene and 0.25 g. of copper chromite catalyst in a glass liner at initial pressure of 1700–1900 lb. a hydrogen uptake calculated for the tetrahydride stage was reached in fifteen minutes at 190°, in one hour at 160°, and, using 30 cc. of absolute alcohol as solvent, in one and one-half hours at 108°. There was no significant difference in the reaction mixtures obtained. In the experiment conducted at 108° the collected product when crystallized from alcohol gave in the first crop 1.8 g. of long, spar-like needles of *s*-hexahydropyrene. The recrystallized material melted at 133.8–134.4° and showed no depression when mixed with a purified sample of the hydrocarbon (m. p. 133–134°) prepared by reduction with sodium and amyl alcohol.[16] A second crop of flaky crystals (1.3 g.) melted at 98–102° and on treatment with picric acid in alcohol afforded first 0.45 g. of red pyrene picrate, m. p. 218–220°. A more soluble picrate crystallized from benzene–ligroin as orange needles, m. p. 146–147° (1.6 g.), and afforded a hydrocarbon (0.35 g.) crystallizing from alcohol in small plates, m. p. 103–105°. This corresponds to the substance isolated by Coulson[15] (m. p. 106°, picrate 148°) and regarded as *as*-**tetrahydropyrene**. A third crystallizate (1.5 g.) melting at 87–93.5° was not identified.

Summary

9-Methyl-3,4-benzpyrene has been synthesized by application of the Scholl ring closure, with subsequent zinc dust distillation, to the benzoyl derivative of 8-methylperinaphthane. The intermediate hydrocarbon was obtained in good yield by synthesis from α-chloromethylnaphthalene and ethyl methylmalonate.

Observations are reported concerning the ozonization and hydrogenation of pyrene.

CONVERSE MEMORIAL LABORATORY
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RECEIVED MAY 20, 1940

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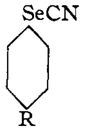
[23] Observations in our laboratory fail to confirm the high m. p. (156°, corr.) for purified pyrene reported by Winterstein, Schön and Vetter, *Z. physiol. Chem.*, **230**, 158 (1934). The most extensively purified sample used by Baxter and Hale, THIS JOURNAL, **59**, 506 (1937), in their atomic weight work was found by Dr. E. B. Hershberg to melt at 150.5–150.8°, corr. Dr. Hershberg subsequently prepared a better, sulfur-free sample by fusion of yellow commercial pyrene with maleic anhydride, distillation, treatment with alkali and then with sodium, and crystallization. The sample was colorless and melted at 150.9–151.1°, corr.

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Organoselenium Compounds. II. Derivatives of Phenylseleninic Acid and Phenylseleninamide

BY C. KENNETH BANKS[1] AND CLIFF S. HAMILTON

In a previous paper[2] the preparation of several series of diphenylselenium dihydroxides and diphenylselenides was reported. This study has been continued into other valencies of selenium, including the diselenides, seleninic acids and selenonic acids. The three series of derivatives considered were the *p*-nitro, acetamino and amino compounds.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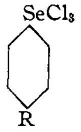
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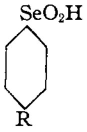
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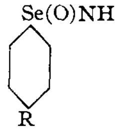
IV

Selenium was introduced into the benzene nucleus by Bauer's modification[3] of the Sandmeyer reaction, giving the selenocyanate (I). *p*-Nitrophenylselenocyanate was prepared by the procedure of Bauer[3] and *p*-acetaminophenylselenocyanate by that of Challenger and Peters.[4] The product reported by Bauer was found to contain an impurity which could be removed by solution in cold concentrated nitric acid and reprecipitation with water. *bis*-(4-Nitrophenyl) diselenide was prepared by the method of Behagel and Siebert[5] and the corresponding acetamino compound was formed by a reaction similar to the method introduced by Behagel and Rollmann.[6] *bis*-(4-Aminophenyl) diselenide had been made by Keimatsu and Satoda[7] from *p*-nitrophenylselenocyanate but it was more conveniently prepared from *bis*-(4-nitrophenyl) diselenide by catalytic reduction.

The seleninic acids (III) were obtained by the oxidation of the selenocyanate to the selenium trichloride (II) and subsequent hydrolysis.[3] Formation of amides of seleninic acids (IV) has never been reported, so particular conditions, starting products and reagents were necessary in each case.

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[1] Parke, Davis and Company Fellow.

[2] C. K. Banks and C. S. Hamilton, THIS JOURNAL, **61**, 2306 (1939).

[3] Bauer, *Ber.*, **46**, 93 (1913).

[4] Challenger and Peters, *J. Chem. Soc.*, 1375 (1928).

[5] Behagel and Siebert, *Ber.*, **66**, 708 (1933).

[6] Behagel and Rollmann, *J. prakt. Chem.*, **123**, 326 (1930).

[7] Keimatsu and Satoda, *J. Pharm. Soc. Japan*, **56**, 600 (1936).

TABLE I

COMPOUNDS AND PROPERTIES

	Compound	Color	M. p., °C.	Yield, %	Formula	Selenium, %[a]	
						Calcd.	Found
1	*bis*-(4-Acetaminophenyl) diselenide	White	143 dec.	83	$C_{16}H_{16}O_2N_2Se_2$	37.1	37.1
2	*bis*-(4-Aminophenyl) diselenide	White	80 dec.	100	$C_{12}H_{12}N_2Se_2$	46.2	46.1
3	4-Acetaminophenylselenium trichloride	Lt. yellow	161 dec.	60	$C_8H_8ONSeCl_3$	24.7	24.8
4	4-Acetaminophenylseleninic acid	White	109 dec.	32	$C_8H_9O_3NSe$	32.1	32.0
5	4-Nitrophenylseleninamide	Yellow	183 dec.	50	$C_6H_6N_2O_3Se$	33.9	34.0
6	4-Acetaminophenylseleninamide	Lt. brown	211 dec.	30	$C_8H_{10}O_2N_2Se$	32.2	32.3
7	4-Aminophenylseleninamide hydrochloride	White	200 dec.	14	$C_6H_8NOSeHCl$	35.5	35.4
8	4-Nitrophenylselenonic acid tetrahydrate	Yellow	113–115	95	$C_6H_5NO_6 \cdot 4H_2O$	24.5	24.5

[a] For the method of analysis see under reference 2.

The stability of these types of selenium compounds seemed to depend chiefly on the para substituent. All of the nitro compounds were extremely stable. The acetamino compounds were fairly stable, the stability decreasing with increasing valence of the selenium, varying from a week to six months. The amino compounds are all unstable, decomposing within a few days to a week.

Experimental

(1) ***bis*-(4-Acetaminophenyl) Diselenide.**—Ten grams of *p*-acetaminophenylselenocyanate was dissolved in a minimum of warm alcohol and an excess of concd. aq. ammonia added. After cooling and diluting with water, the product was filtered off, washed with water, recrystallized from alcohol and dried.

(2) ***bis*-(4-Aminophenyl) Diselenide.**—Forty grams of *bis*-(4-nitrophenyl) diselenide was dissolved in acetone and reduced with molecular hydrogen at 40 pounds pressure (2.67 atm.) using Raney nickel catalyst. After reduction ceased the catalyst was filtered off, the solvent removed by evaporation under reduced pressure and 2 *N* hydrochloric acid added. The solution was charcoaled and the amine reprecipitated with sodium hydroxide.

(3) **4 - Acetaminophenylselenium Trichloride.**—Ten grams of *p*-acetaminophenylselenocyanate was suspended in 50 ml. of chloroform and a stream of chlorine gas passed through the solution until reaction ceased. The solid trichloride was filtered off and recrystallized from fresh chloroform. The compound was not stable, decomposing within a week.

(4) **4-Acetaminophenylseleninic Acid.**—Five grams of the above trichloride was suspended in dry ether and 95% alcohol added until the trichloride had decomposed. The solution was warmed and allowed to cool. The product crystallized in white plates that decomposed readily. The substance was very soluble in water.

(5) **4-Nitrophenylseleninamide.**—Thionyl chloride (2.5 g.) was added slowly to *p*-nitrophenylseleninic acid (5 g.). The paste formed was then added to an excess of concd. ammonia. The insoluble material formed was filtered off and digested with hot alcohol to remove any diselenide formed. Nearly all of the unreacted starting material was recovered by acidification of the ammonia filtrate.

(6) **4-Acetaminophenylseleninamide.**—Five grams of *p*-acetaminophenylselenocyanate was dissolved in 10 ml. of concd. nitric acid at 0° and allowed to stand for fifteen minutes. The solution was then poured into 25 ml. of concd. ammonia with 25 ml. of alcohol. After standing for several hours, the solution was warmed, evaporated nearly to dryness and water added. The insoluble portion was filtered off and recrystallized from alcohol. The compound was stable for several months.

(7) **4-Aminophenylseleninamide Hydrochloride.**—Five grams of *bis*-(4-aminophenyl) diselenide was dissolved in 10 ml. of 10 *N* nitric acid at $-5°$ and the solution allowed to stand a half hour. This was then poured into a solution made from 35 ml. of concd. aq. ammonia and an equal volume of alcohol. After standing for several hours, the solution was filtered and the alcohol removed by evaporation. The water solution was extracted several times with ether, the ether extracts combined and dried over calcium chloride. The dry ether solution, on saturation with dry hydrogen chloride gas, precipitated the amine hydrochloride in a very pure condition. The product began to decompose within a day and the selenium was entirely cleaved within several weeks.

(8) **4-Nitrophenylselenonic Acid Tetrahydrate.**—4-Nitrophenylseleninic acid (5 g.) was dissolved in 20 ml. of fuming nitric acid, a trace of hydrochloric acid added and the solution boiled until all fumes of nitric oxide were removed. On cooling, the acid tetrahydrate crystallized in yellow tetragonal crystals which were filtered off, washed with anhydrous ether and dried in a vacuum desiccator. The product decomposes in water solutions and has great oxidative power.

Summary

1. Three substituted phenylseleninamides were prepared. This is the first record of amides of organoselenium acids.

2. Several other new organoselenium compounds were prepared by standard synthetic procedures.

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