Dibenzothiophene and 4-N-Ethylcarbazolyllithium; and 4-Dibenzothienyllithium and N-Ethylcarbazole.—The solution of 4-N-ethylcarbazolyllithium prepared by refluxing 0.045 mole of *n*-butyllithium in 200 cc. of ether for twenty hours with an equivalent of N-ethylcarbazole was shown to be free of *n*-butyllithium by two tests. The first of these established the absence of *n*-valeric acid when an aliquot was carbonated. The second was a negative color test II.[6] Then 0.045 mole of dibenzothiophene was added and refluxing was continued for six hours. Oxidation of the acid (which gave no nitrogen test) yielded 20% of 4-dibenzothiophenecarboxylic-5-dioxide acid, but no 4-N-ethylcarbazolecarboxylic acid.

From a corresponding reaction between 4-dibenzothienyllithium and N-ethylcarbazole, there was isolated 46% of 4-dibenzothiophenecarboxylic acid but no 4-N-ethylcarbazolecarboxylic acid.

Metalation of Dibenzofuran by Ethyllithium, *n*-Propyllithium and *n*-Butyllithium.—In order to determine the more effective metalating agent, a preliminary examination was made of the extent of metalation of dibenzofuran by these RLi compounds under corresponding conditions. It was found that the highest yield (63%) of 4-dibenzofurancarboxylic acid,[7] subsequent to carbonation, was obtained when *n*-butyllithium was used. With *n*-propyllithium the yield was 61%, and with ethyllithium the yield was 50%. This order is in general agreement with that noted earlier for the ethyl and *n*-butyl compounds in a study[8] concerned largely with branched-chain alkyllithium compounds.

---

(6) Gilman and Swiss, THIS JOURNAL, **62**, 1847 (1940).

(7) A by-product of all the carbonations was bis-(4-dibenzofuryl) ketone, the yield of which reached 7.8% in some experiments.

(8) Gilman, Moore and Baine, THIS JOURNAL, **63**, 2479 (1941).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED FEBRUARY 5, 1945

The Unit Cell and Space Group of Potassium Tetrachlorozincate

BY HAROLD P. KLUG AND GEORGE W. SEARS, JR.

In the studies of halogen complexes with certain elements under way in this Laboratory, potassium tetrachlorozincate, K_2ZnCl_4, was investigated with the hope that it might supply information concerning the coördination of chlorine around zinc, and the nature of the groups present in the crystalline tetrachlorozincates. Although the compound proved unsatisfactory for the complete study, certain results were obtained which are reported in this communication.

The salt was prepared by crystallization from aqueous solutions of mixtures of the component salts, KCl and $ZnCl_2$, as described by Marignac,[1] who made numerous angular measurements on the crystals. Steinmetz[2] made optical measurements on it and observed its cleavage parallel to (010). Groth[3] described the crystals as prismatic along the c axis, and belonging to the rhombic bipyramidal class. He reported the axial ratios $a:b:c = 0.7177:1:0.5836$, and the density to be 2.297. The identity of the prepared salt was verified by angular measurements in the [$hk0$] zone, and by chemical analysis for zinc and chlorine. *Anal.* Calcd. for K_2ZnCl_4: Zn, 22.91; Cl, 49.70. Found: Zn, 22.80, 22.77; Cl, 49.54, 49.55. A redetermination of the density was made by suspension in a liquid of equal density. Three separate determinations gave an average value of 2.364, which is somewhat higher than the value reported by Groth.

Preliminary layer line measurements on rotation photographs led to the cell edges $a_0 = 8.90$ Å., $b_0 = 12.26$ Å., $c_0 = 7.28$ Å., and a cell containing 4 K_2ZnCl_4. These values correspond to axial ratios $a:b:c = 0.726:1:0.5935$ in good agreement with Groth's values. However, closer inspection of the photographs about a revealed what appeared to be faint spots at distances of one-third and two-thirds that of the obvious layer lines. Much longer exposures definitely revealed fainter layer lines which necessitated the tripling of a_0 and the volume of the cell. The final values are $a_0 = 26.70$ Å., $b_0 = 12.26$ Å., $c_0 = 7.28$ Å., and 12 K_2ZnCl_4 per cell. The true axial ratios from these values are: $a:b:c = 2.178:1:0.5935$.

Laue photographs, analyzed by means of gnomonic projections, showed all types of pyramid planes to be present in the first order. The underlying lattice is thus simple primitive. The only first-order prism absence noted was ($h0l$) when h is odd. The space group symbol is thus *Pmam* if the crystal has a center of symmetry. A pyroelectric test by the method of Martin[4] revealed a decided positive pyroelectric effect with the c axis the polar axis. The true space group symbol then is *Pma*2 and the space group is $C_{2v}^{4} - Pma$.[5]

With a non-centrosymmetrical space group and a twelve molecule cell it did not seem profitable to pursue the investigation further.

---

(1) Marignac, *Ann. Min.*, [5] **12**, 15 (1857).

(2) Steinmetz, *Z. Krist.*, **56**, 166 (1921).

(3) Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Vol. I, p. 342.

(4) Martin, *Min. Mag.*, **22**, 519 (1931).

(5) "International Tables," Vol. I, p. 105.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINNESOTA

RECEIVED FEBRUARY 13, 1945

Schiff Bases from Benzaldehyde and *o*-Aminophenols

BY L. CHAS. RAIFORD[1] AND JACOB LINSK[2]

Ehmke[3] condensed ortho-aminophenol with a number of substituted benzaldehydes and prepared derivatives. In the present work the condensation reaction was extended and eight Schiff bases were prepared from benzaldehyde and substituted *o*-aminophenols. In the preparation of derivatives some tendency to hydrolysis was noted. 2-Benzalamino-4-bromophenol and 6-ben-

---

(1) Deceased Jan. 8, 1944.

(2) (a) Extracted from the Master's thesis of Jacob Linsk, August, 1941. (b) Present address: Research laboratory, George A. Breon and Co., Kansas City, Missouri.

(3) Ehmke, Master's thesis, State University of Iowa, 1940.

Aminophenol	Schiff bases and derivs.	M. p., °C. (uncor.)	Formula	Analyses, % Calcd.	Analyses, % Found
2-Amino-4-bromo-phenol[4]	2-Benzalamino-4-bromophenol[5]	113	$C_{13}H_{10}ONBr$	Br, 28.9	28.8
2-Amino-4,6-dibromophenol	2-Benzalamino-4,6-dibromophenol	143	$C_{13}H_9ONBr_2$	Br, 45.0	45.1
	Acetate	121	$C_{15}H_{11}O_2NBr_2$	Br, 40.3	40.3
2-Amino-4-chloro-phenol[4]	2-Benzalamino-4-chlorophenol	92	$C_{13}H_{10}ONCl$	Cl, 15.3	15.3
	Benzoate	155	$C_{20}H_{14}O_2NCl$	Cl, 10.6	10.1
2-Amino-4,6-dichlorophenol	2-Benzalamino-4,6-dichlorophenol	152	$C_{13}H_9ONCl_2$	Cl, 26.6	26.4
	Acetate	121	$C_{15}H_{11}O_2NCl_2$	Cl, 23.0	22.8
6-Amino-4-chloro-*o*-cresol	6-Benzalamino-4-chloro-*o*-cresol	125	$C_{14}H_{12}ONCl$	Cl, 14.4	14.3
	Benzoate	160	$C_{21}H_{16}O_2NCl$	Cl, 10.1	9.6
6-Amino-4-bromo-*m*-cresol	6-Benzalamino-4-bromo-*m*-cresol[6]	116	$C_{14}H_{12}ONBr$	Br, 27.6	27.7
6-Amino-2,4-dibromo-*m*-cresol	6-Benzalamino-2,4-dibromo-*m*-cresol	154	$C_{14}H_{11}ONBr_2$	Br, 43.3	43.3
	Acetate	180	$C_{14}H_{14}O_2NBr_2$	Br, 38.9	38.8
2-Amino-4-nitrophenol.	2-Benzalamino-4-nitrophenol	189	$C_{13}H_{10}O_3N$	N, 11.57	11.86
	Acetate	100	$C_{14}H_{12}O_4N_2$	N, 9.86	10.16

zalamino-4-bromo-*m*-cresol were split in the course of acetylation. The N-acetyl derivatives of the corresponding *o*-aminophenols were isolated. Substituents in the *o*-aminophenol molecule offered no hindrance in the condensation reaction. Picramic acid or its sodium salt could not be condensed with benzaldehyde.

The bases were prepared by mixing equimolecular quantities of benzaldehyde and the appropriate amine in an Erlenmeyer flask. A condenser was attached and the flask was set in a hot water-bath. The reaction product set solid in a short while. It was broken up, dissolved in the appropriate solvent, usually methanol or ethanol, filtered through boneblack and crystallized. The derivatives were prepared in the usual manner. The reaction products were poured into water and the resulting solids crystallized from methanol. The yields of the Schiff bases varied from 43% in one case to 95%. All of the aminophenols except the last one were synthesized according to known methods. A commercial preparation of 2-amino-4-nitrophenol was used. The compounds melted within one degree and the lower limit of the melting point is recorded in the table. The halogen analyses were made by the semi-micro Parr bomb method. The nitrogen analyses were made by the micro-Dumas method.

CHEMISTRY DEPARTMENT
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA
RECEIVED JANUARY 25, 1945

---

[4] The best procedure for the preparation of these amines from the corresponding nitro compounds was reduction of the latter with alkaline sodium hydrosulfite according to the method described by Alexander (Doctor's dissertation, Iowa, 1939) for the reduction of 2-nitro-4-bromophenol. The yields were 84 and 82%, respectively.

[5] Attempted acetylation of this Schiff base with acetic anhydride and sodium acetate yielded a product which gave an analysis that was 4% too high in bromine. In a second experiment 4 g. of the Schiff base was dissolved in 5 cc. of pyridine and 10 cc. of acetic anhydride was added. The solution was warmed and allowed to stand overnight. When it was poured into ice water a dark oil separated, which on shaking gave 3.8 g. of a light brown solid. Recrystallization from dilute methanol gave small plates, m. p. 175–175.5°, 81% yield. Analysis was satisfactory for the acetate of 2-amino-4-bromophenol. *Anal.* Calcd. for $C_8H_8O_2NBr$: Br, 34.7. Found: Br, 34.7. The compound was insoluble in acid and soluble in dilute sodium hydroxide. Shutt, *J. prakt. Chem.*, [2] 32, 63 (1885), reported a m. p. of 177° for a compound which he considered to be 2-acetylamino-4-bromophenol.

[6] Attempted acetylation of this compound with acetic anhydride in pyridine solution gave colorless needles from methanol (94% yield) m. p. 190°. The compound was insoluble in acid and soluble in dilute sodium hydroxide. Analysis was acceptable for a compound whose formula corresponds to that of 6-acetylamino-4-bromo-*m*-cresol. *Anal.* Calcd. for $C_9H_{10}O_2NBr$: Br, 32.8. Found: Br, 32.4.

The Borates of 2,3-Butylene Glycol

BY S. A. MORELL[1] AND E. C. LATHROP[2]

Recently R. E. Rippere and V. K. LaMer[3] have called in question the preparation of certain complex di-orthoborates by Dupire[4] using the azeotropic esterification of boric acid with various glycols. In connection with a study of the conversion of 2,3-butylene glycol to butadiene, two borates of *meso*-2,3-butylene glycol were prepared by Dupire's method, the first of which proved to be identical with the simple mono-acid borate described by Rippere and LaMer, and the other corresponding to the borate described by Dupire.

Mono-acid Borate of 2,3-Butylene Glycol.—A 1:1 mixture of 10 moles each of *meso*-2,3-butylene glycol and orthoboric acid and 1 liter of benzene was heated in a 3-liter flask equipped with a 30 × 2.5 cm. Vigreaux column and a gravity separator for continuous azeotropic removal of the water. After twenty hours the formation of water had ceased, 400 ml. being collected (theoretical, 360 ml.). On distillation *in vacuo*, a main fraction of 674 g., b. p. 129–134° (4 mm.), was obtained or 58% of that required by theory. When redistilled at atmospheric pressure, about 90% was recovered in the fraction b. p. 266–269° (uncor.). When dissolved in water or in solutions between *p*H 1 and 13, this ester was immediately and completely hydrolyzed as shown by titration, in the presence of glycerol, of the liberated boric acid. The neutral equivalent required by theory is 115.9; found, 113.5. When a 2:1 molar ratio of boric acid to the glycol was used in the esterification, the same product was obtained in a yield of 53%, 45% of the boric acid remaining undissolved.

Di-orthoborate of *meso*-2,3-Butylene Glycol.—When the reaction was conducted as described above, but with the boric acid decreased to 413.5 g. (2:3 molar ratio of boric acid to the glycol), the water formed amounted to 354 ml. (theoretical, 361 ml.). On distillation, a main fraction of

---

[1] Present address: Pabst Brewing Co., Milwaukee, Wis.

[2] Head, Agricultural Residues Division.

[3] R. E. Rippere and V. K. LaMer, *J. Phys. Chem.*, **47**, 212 (1943).

[4] A. Dupire, *Compt. rend.*, **202**, 2086 (1936).