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	$C_{16}H_{14}O_2NBr_2$	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	$C_{15}H_{12}O_4N_2$	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.

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[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

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

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

857 g., b. p. 290–292° (uncor.), was obtained or a yield of 90%. This too hydrolyzed completely when dissolved in water.

Anal. Calcd. for $C_{12}H_{24}O_6B_2$: C, 50.40; H, 8.46; neut. eq., 143.0. Found: C, 49.95; H, 8.42; neut. eq., 144.5.

Discussion.—These two esters, as might have been expected from their formulas, exhibited marked differences in their chemical reactions and physical properties. With metallic sodium, for example, the acid borate reacted vigorously on heating, whereas the orthoborate showed practically no reaction. In acetone solution, the acid borate appeared to form a true salt with ammonia, whereas the orthoborate yielded a gelatinous complex. The esters may be distilled at atmospheric pressure without decomposition. At room temperature, the orthoborate is a sirup of the consistency of glycerol, whereas the acid borate is so viscous that it hardly flows.

It should be pointed out that the above diorthoborate, having been prepared from the *meso* form, may represent a new substance, since Dupire makes no mention as to whether in his preparation a single isomer or a mixture of the isomers was used.

Rippere and LaMer's[3] failure to obtain the Dupire-type[4] glycol borates may have been due to the fact that when the esterification is conducted azeotropically in benzene solution, a much more uniform reaction occurs at a lower temperature than when the reactants are merely mixed and heated to drive off the water.

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The Vapor Pressure of Trimethylamine from 0 to 40°

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In the course of a study of the properties of the simpler aliphatic amines near room temperature we have measured the vapor pressure of trimethylamine at a number of temperatures between 0 and 40°, since no published data could be found covering this range.

The purification of the compound has been described previously.[1] Since the chemical treatment does not take care of dissolved gases, each sample after desiccation was thoroughly degassed by repeated freezing and melting with evacuation. This process was continued until the sample had evaporated to approximately half of its original volume. As a check on the purity of the amine, its vapor pressure was measured at the ice-point, the vapor then being allowed to expand into a volume approximately ten times as great as before and the pressure again measured. If a significant difference in vapor pressure was found, the degassing process was repeated until results concordant to at least 1 mm. were obtained.

The samples were transferred by vacuum distillation to an isotensiscope equipped with a magnetic stirrer, which served to break the surface of the liquid about twice a second. As a check on possible contamination during transfer, the vapor pressure at the ice-point was measured again, and in every case checked, within less than a millimeter, the value found when the sample was directly connected to the manometer.

At each temperature care was taken to allow sufficient time for equilibrium to be established, as evidenced by a steady reading for at least half an hour while the liquid was being agitated. The mercury levels in the isotensiscope were adjusted to within 0.5 mm. of each other, and the levels in the manometer then read with a Societé Génévoise cathetometer. Since some of the preliminary measurements were made with a Gaertner cathetometer, the two instruments were checked against each other and found to agree within better than 0.5 mm. over the whole scale. For heights greater than 1000 mm., a meter stick was used, and later checked against the cathetometer scale.

The barometric pressure was taken from an open manometer which was read with the same cathetometer as above. The diameters of the reservoir and tube of this manometer were the same as those of the main manometer, to cancel out any bore correction. Brass scale corrections were applied to all readings.

Temperatures were maintained constant to ±0.02°, the absolute value being obtained to 0.01° by comparing the thermometers used with a platinum resistance thermometer calibrated at the ice-point.

The corrected observed pressures are shown in Table I, as averaged values for all readings.

TABLE I

VAPOR PRESSURES OF TRIMETHYLAMINE

T, °C.	$P_{\text{obs.}}$ mm.	$P_{\text{obs.}} - P_{\text{calcd.}}$, %[a]	$P_{\text{obs.}} - P_{\text{calcd.}}$ %[b]
0	683	0.4	0.6
15	1189	0.8	−0.3
20	1415	1.4	0
25	1663	1.2	−0.2
30	1946	1.4	−0.2
35	2266	1.5	0
40	2621	1.5	0.2

[a] Equation (1), ref. 2. [b] Equation (1), this paper.

The largest difference between samples was less than 1%, the average deviation from the mean being 0.3%. The over-all accuracy is about 0.5%.

After these measurements were completed, the results of a very careful study by Aston and coworkers of the vapor pressure of trimethylamine at temperatures between −80 and +3° appeared,[2] together with an empirical equation

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(1) E. Swift, Jr., THIS JOURNAL, **64**, 115 (1942).

(2) J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen and H. F. Zuhr, *ibid.*, **66**, 1171 (1944).