alone or admixed with material prepared by the other route.

*Anal.* Calcd. for $C_{15}H_{14}N_2OS$: N, 10.36. Found: N, 10.08.

**N-(*m*-Tolyl)-N'-phenylthiourea.**—Prepared by mixing and allowing to spontaneously react *m*-tolyl isothiocyanate and aniline, or *m*-toluidine and phenyl isothiocyanate; m. p., after three recrystallizations from benzene–Skellysolve B, 109–110°, alone or when admixed. Otterbacher and Whitmore[3] allowed *m*-toluidine and phenyl isothiocyanate to react in alcohol and obtained a product of the correct nitrogen analysis but with m. p. 94°.

*Anal.* Calcd. for $C_{14}H_{14}N_2S$: C, 69.39; H, 5.82; N, 11.56; S, 13.23. Found: C, 69.53; H, 5.86; N, 11.34; S, 13.47.

(3) Otterbacher and Whitmore, THIS JOURNAL, **51**, 1909 (1929).

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## Substituted Salicylaldehydes and Derivatives[1]

For the study of some special physical properties of chelated metal salts of certain Schiff bases of aldehydes a number of substituted salicylaldehydes and their derivatives were prepared, purified and analyzed. The results are presented in Table I.

TABLE I

| Salicylaldehyde | Method[9] | Yield, % | M. p., °C.[6] | Analyses, % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|
| 3-Methyl[2] | A | 6 | En, 115 | 73.0 | 72.9 | 6.75 | 6.63 |
| 4-Methoxy,[3] methyl ether | D | >50 | DNPH, 245 | 52.0 | 52.2 | 4.05 | 4.10 |
| 5-Methoxy[4] | A | 16 | DNPH, 211–212 | 59.8 | 60.0 | 4.98 | 5.02 |
| 3-Chloro[5] | C | 40 | En, 150–152 | 57.0 | 57.0 | 4.15 | 4.27 |
| 5-Chloro[2] | [10] | <5 | En, 174–175 | 57.0 | 57.1 | 4.15 | 4.22 |
| 3-Iodo | B | 5[8] | Cu salt | 30.1 | 30.9 | 1.44 | 1.57 |
| 3-Cyano | [11] | 5–10 | 114 | 65.3 | 65.2 | 3.4 | 3.4 |
| 3-Formyl, oxime[7] | A | <5 | NPH, 269–271 | 56.0 | 56.6 | 4.0 | 4.0 |
| 3-Phenyl | A | 13 | 50 | 78.7 | 78.3 | 5.05 | 5.16 |
| 5-*t*-Butyl | A | ~10 | En, 165–167.5 | 75.8 | 76.1 | 8.42 | 8.34 |
| 3-Isopropyl-6-methyl[2] | A | 16 | En, 112–113 | 75.8 | 75.3 | 8.42 | 8.38 |
| 6-Isopropyl-3-methyl[2] | A | 20 | En, 139–140 | 75.8 | 75.4 | 8.42 | 8.08 |

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(1) The work reported here was done under contract OEM sr/276 between the National Defense Research Committee and the University of California during the period April, 1942, to April, 1944. For the primary interest of the project, see papers I through VII, THIS JOURNAL, **69**, 1886 (1947).

(2) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(3) L. Gattermann, *Ber.*, **31**, 1149 (1898).

(4) F. Tiemann and W. H. M. Muller, *ibid.*, **14**, 1990 (1881).

(5) H. H. Hodgson and T. A. Jenkinson, *J. Chem. Soc.*, 1740 (1927).

(6) En = ethylenediamine Schiff base; DNPH = 2,4-dinitrophenylhydrazone; NPH = *p*-nitrophenylhydrazone.

(7) H. Voswinckel, *Ber.*, **15**, 2023 (1892).

(8) There was also obtained a 13% yield of 3-iodo-4-hydroxybenzaldehyde.

(9) A = Duff; B = Reimer–Tiemann, *Ber.*, **9**, 824 (1876); C = Kolbe–Schmitt and NaHg reduction, THIS JOURNAL, **68**, 2502 (1946); D = Ferguson, *Chem. Revs.*, **38**, 230 (1946).

(10) Chlorination with sodium hypochlorite.

(11) From 3-methylsalicylaldehyde to the oxime, m. p. 97–99°, acetylation and bromination to 2-acetoxy-3-cyanobenzal bromide, m. p. 98–99°, and hydrolysis with sodium carbonate solution. DNPH, m. p. 270° (dec.)

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## *o*-Nitrophenyl-β-D-galactopyranoside and its Tetraacetate

These derivatives of D-galactose were prepared for use as chromogenic substrates for studies on bacterial β-galactosidases.[1]

***o*-Nitrophenyl-β-D-galactopyranoside Tetraacetate.**—The procedure of Glaser and Wulwek[2] for the corresponding glucose derivative was employed. Forty-two grams of *o*-nitrophenol was dissolved in a solution of 16.8 g. of sodium hydroxide in 420 ml. of water. To this was added a solution of 88 g. of tetraacetyl-α-D-galactopyranosyl bromide[3] in 620 ml. of acetone. After standing at room temperature for five hours the solvent was removed by distillation under reduced pressure. The product appeared as long needles which caused considerable bumping. It was filtered off and the concentration continued until no more crystals formed. After recrystallization from 95% ethanol 56 g. was obtained, m. p. 172–172.5°, $[\alpha]^{18}D$ + 69.9° (*c*, 1.9, chloroform).

*Anal.* Calcd. for $C_{20}H_{23}O_{12}N$: C, 51.1; H, 4.90. Found: C, 51.0; H, 4.96.

***o*-Nitrophenyl-β-D-galactopyranoside.**—The free glycoside was obtained by catalytic deacetylation. One gram of the above product was suspended in 50 ml. of absolute methanol and 1 ml. of 0.4 *N* barium methoxide solution was added. The mixture was refrigerated and shaken periodically. After four hours a clear solution resulted and soon thereafter crystals in the form of long hair-like needles separated. After twenty-four hours the reaction mixture was concentrated under reduced pressure and a quantitative yield of *o*-nitrophenyl-β-D-galactopyranoside was obtained. The melting point after two recrystallizations from absolute ethanol was 193–194°, $[\alpha]^{18}D$ −51.9° (*c*, 1.0, water).

*Anal.* Calcd. for $C_{12}H_{15}O_8N$: C, 47.8; H, 4.98. Found: C, 48.1; H, 5.20.

(1) By Dr. J. Lederberg, Department of Genetics, University of Wisconsin.

(2) Glaser and Wulwek, *Biochem. Z.*, **145**, 514 (1934); see also Babers and Goebel, *J. Biol. Chem.*, **105**, 473 (1934); Aizawa, *Enzymologia*, **6**, 321 (1939).

(3) Haynes and Todd, *J. Chem. Soc.*, 303 (1950).

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## 5-Chloro-2-pyrimidinethiol

**5-Chloro-2-pyrimidinethiol.**—A solution of 13 g. (0.33 mole) of sodium hydroxide in 400 cc. of methanol was saturated with hydrogen sulfide. Fifty grams (0.33 mole) of 2,5-dichloropyrimidine[1] was added and the mixture was refluxed for fifteen minutes. Violent bumping followed

(1) English, Clark, Shepherd, Marson, Krapcho and Roblin, THIS JOURNAL, **68**, 1039 (1946).