Procedure.—Benzaldehyde (0.4 mole), the anhydride (0.6 mole), and the calcium hydride (0.6 mole) were refluxed for seven hours and then water was added to decompose the unreacted hydride. The mixture was then worked up in the usual manner.

The yields of cinnamic acids obtained with acetic, propionic, and *n*-butyric anhydrides were, respectively, 8.3, 9.1 and 7.4%. Increasing the molar ratio of the aldehyde (0.7 mole) increases the yield to 16.4% in the reaction with propionic anhydride. Varying the anhydride concentration did not affect the yield, but increasing the calcium hydride ratio produced increased amounts of the unsaturated acids.

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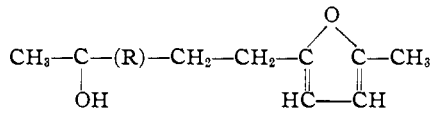
RECEIVED FEBRUARY 27, 1950

NEW COMPOUNDS

2-Substituted-4-(5-methyl-2-furyl)-2-butanols[1]

A series of compounds of the formula



has been prepared (Table I). The preparation of 4-(5-methyl-2-furyl)-2-butanol, a typical example, was carried out in the following manner. To a solution of *p*-tolylmagnesium bromide prepared from 6.1 g. of magnesium and 42.8 g. of *p*-bromotoluene was added dropwise during twenty-five minutes 22.8 g. (0.15 mole) of 4-(5-methyl-2-furyl)-2-butanone[2] dissolved in 75 ml. of ether, maintaining the temperature below 20°. After stirring for one hour at room temperature, a qualitative test for the Grignard reagent[3] was made to assure that an excess had been present. Decomposition was effected with crushed ice and 200 ml. of a saturated ammonium chloride solution and ether removed on a water-bath. The resulting product was steam distilled to remove toluene and 4,4′-bitolyl, the organic layer separated and the aqueous layer extracted with ether. The solvent was distilled from the dried combined ether solutions and the residue distilled at reduced pressure. The yield of light yellow oil, b. p. 144.5–146° (1 mm.), d^{25}_4 1.0451, was 28.4 g. (77.6%). The molecular refraction was calculated to be 72.52 ($M^{25}D$) and the value found was 72.84.

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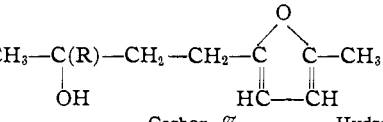
RECEIVED MAY 5, 1950

TABLE I

2-SUBSTITUTED 4-(5-METHYL-2-FURYL)-2-BUTANOLS 

R	Boiling point °C.	Boiling point Mm.	Yield, %	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Butyl	101–106	1	75.6	1.4740	$C_{13}H_{22}O_2$	74.24	73.83	10.54	10.35
Phenyl	151–154	9	73.5	1.5386	$C_{15}H_{18}O_2$	78.23	78.08	7.88	8.05
Cyclohexyl[a]	131–161	1	18.9	1.5010	$C_{15}H_{24}O_2$	76.22	76.03	10.24	10.38
Benzyl	154–157	2	83.9	1.5347	$C_{16}H_{20}O_2$	78.65	78.34	8.25	8.36
p-Tolyl	144.5–146	<1	77.6	1.5355	$C_{16}H_{20}O_2$	78.65	78.31	8.25	8.08
1-Naphthyl	219–219.5	9	84.8	1.601[b]	$C_{19}H_{20}O_2$	81.40	81.10	7.19	6.95

[a] Yield, refractive index and analytical data are given for a redistilled product. [b] $n^{28}D$ (Fischer refractometer) for supercooled liquid.

Aryl Isothiocyanates and Thioureas

***o*-Biphenyl Isothiocyanate.**—Prepared in 24% yield by the procedure (A) of Dains, Brewster and Olander[1]; b. p. 122° (0.04 mm.), $n^{25}D$ 1.6572.

Anal. Calcd. for $C_{13}H_9NS$: C, 73.90; H, 4.29; N, 6.63. Found: C, 73.92; H, 4.15; N, 6.68.

N,N′-Bis-(*o*-biphenyl)-thiourea.—Obtained, in a few per cent. yield, as a by-product in the above preparation; m. p., after two recrystallizations from benzene–Skellysolve C, 142–143°.

Anal. Calcd. for $C_{25}H_{20}N_2S$: C, 78.91; H, 5.30; N, 7.36. Found: C, 79.17; H, 5.61; N, 7.42.

***p*-Diethylaminophenyl Isothiocyanate.**—Prepared in 36% yield by procedure A; b. p. 148° (1.2 mm.); $n^{25}D$ 1.6690.

Anal. Calcd. for $C_{11}H_{14}N_2S$: S, 15.54. Found: S, 15.79.

N,N′-Bis-(*p*-diethylaminophenyl)-thiourea.—Obtained as a minor by-product in the above preparation; m. p., after three recrystallizations from alcohol, 165–166.5°.

Anal. Calcd. for $C_{21}H_{30}N_4S$: C, 68.06; H, 8.16; N, 15.12. Found: C, 68.07; H, 7.87; N, 15.05.

***p,p′*-Methylenebis-(phenyl) Isothiocyanate.**—Prepared by procedure A in 48% yield; m. p., after two recrystallizations from glacial acetic acid, 143–144°.

Anal. Calcd. for $C_{15}H_{10}N_2S_2$: C, 63.80; H, 3.57; N, 9.92. Found: C, 63.96; H, 3.84; N, 10.07.

***p*-(*t*-Amyl)-phenyl Isothiocyanate.**—Prepared in 49% yield by procedure A; b. p. 104° (0.2 mm.).

Anal. Calcd. for $C_{12}H_{15}NS$: C, 70.20; H, 7.36; N, 6.82. Found: C, 70.40; H, 7.30; N, 6.66.

***m*-Acetylphenyl Isothiocyanate.**—Prepared in 76% yield by the procedure of Dyson[2]; b. p. 112° (0.2 mm.); $n^{25}D$ 1.6453.

Anal. Calcd. for C_9H_7NOS: C, 60.99; H, 3.98; N, 7.90. Found: C, 60.77; H, 4.20; N, 7.83.

N-(*m*-Acetylphenyl)-N′-phenylthiourea.—Prepared by mixing and allowing to spontaneously react *m*-acetylphenyl isothiocyanate and aniline, and by warming until homogeneous a mixture of *m*-acetylaniline and phenyl isothiocyanate. In each case the product melted, after recrystallization from benzene–Skellysolve C, at 108–110°,

(1) The work reported in this paper is taken in part from the thesis submitted by Warren J. Murbach to the Graduate School of the University of Kansas City in partial requirements for the degree of Master of Arts.

(2) Alder and Schmidt, *Ber.*, **76B**, 183 (1943).

(3) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(1) Dains, Brewster and Olander, "Organic Syntheses," Coll. Vol. I, Second Ed., 1944, p. 447.

(2) Dyson, "Organic Syntheses," Coll. Vol. I, sec ond ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 65.

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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RECEIVED APRIL 24, 1950

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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BERKELEY, CALIF. MELVIN CALVIN

RECEIVED OCTOBER 3, 1949

(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.)

(12) Chemistry Dept., Howard University, Wash., D. C.

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).

DEPARTMENT OF BIOCHEMISTRY
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MADISON, WISCONSIN KARL PAUL LINK

RECEIVED MAY 25, 1950

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).