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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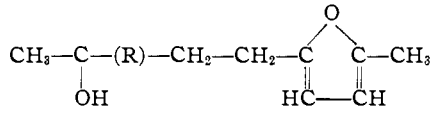
RECEIVED FEBRUARY 27, 1950

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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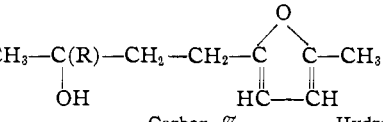
RECEIVED MAY 5, 1950

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.

(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).

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) 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.