

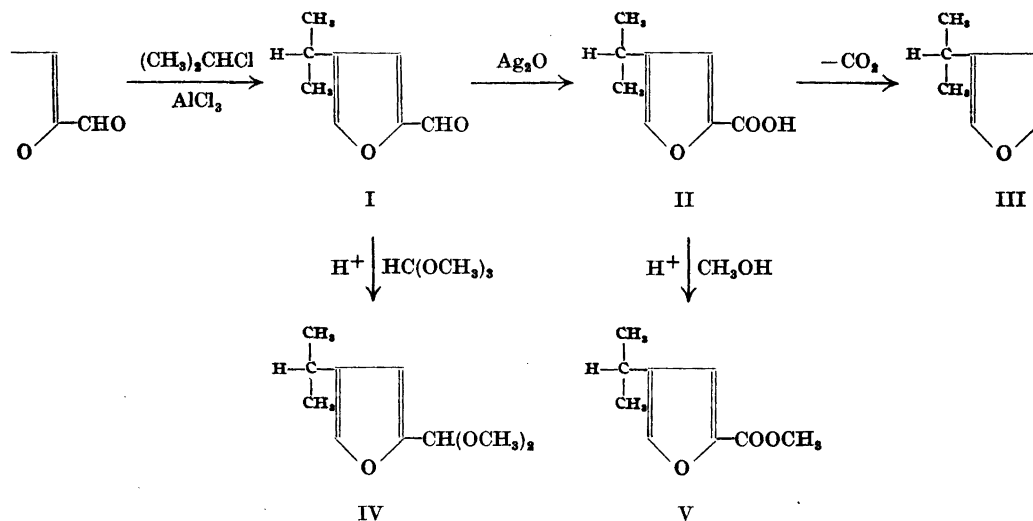
## Short Communications

### Preparation of Some $\beta$ -Isopropylfurans

NIELS ELMING

Centrallaboratoriet, Sadolin & Holmblad A/S,  
Copenhagen, Denmark

In the course of an investigation of the alkoxylation of furans, compounds I-V have been prepared by the sequence of reactions shown below:



The directions of Gilman *et al.*<sup>1-3</sup> were — with some modifications — followed for the preparation of I-III, while IV and V, which are new compounds, were prepared by well-known methods. Gilman *et al.* have determined the structure of I-III. The structure of IV and V

follows from their synthesis and from analyses.

EXPERIMENTAL (Microanalyses by F. Limborg and K. Glens). *4-Isopropyl-2-furaldehyde (I)* (cf. Gilman and Calloway<sup>1</sup>; Gilman, Calloway and Burtner<sup>3</sup>). 242 g of freshly distilled furfural (2.50 moles) and 200 g of isopropyl chloride (2.55 moles) are mixed and added during 1 3/4 hours to a stirred suspension of 405 g of powdered aluminum chloride (3.00 moles) in 1400 ml of carbon disulfide. The reaction flask is cooled occa-

sionally to maintain a gentle reflux. Stirring is continued for 18 hours at room temperature. The mixture is poured on cracked ice with vigorous stirring, and the two resulting layers are separated. The carbon disulfide solution is washed with water, 4 M sodium acetate and 0.8 M sodium hydrogen carbonate and dried with sodium sulfate. The carbon disulfide is

distilled off and the residue distilled under nitrogen.

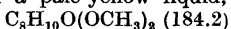
Fraction (g)	B. p. <sub>16</sub>	Colour
1 (82)	< 80°	dark
2 (67)	80°–110°	—
3 (34)	110°–145°	—
residue (71)		—

Fraction 2 is redistilled under nitrogen through a 5 cm column packed with glass helices.

Fraction (g)	B. p. <sub>13</sub>	$n_D^{25}$	Colour
1 (8.0)	55°–90°		dark
2 (1.9)	90°–92°	1.5052	light-brown
3 (37.0)	92°–95°	1.5025	—
4 (4.4)	95°–105°	1.4988	—

Yield (fraction 3) 37.0 g of isopropylfuraldehyde = 11 %. Another distillation through the same column gives 33.0 g = 9.5 %; b. p.<sub>13</sub> = 92°–95°;  $n_D^{25}$  = 1.5032. The colour of this product is also light-brown. Gilman and Calloway<sup>1</sup> obtained a 12 % yield of their product (b. p.<sub>21</sub> = 101°–103°;  $n_D^{25}$  = 1.5041).

*4-Isopropyl-2-furaldehyde dimethyl acetal (IV)*. 18.0 g of isopropylfuraldehyde (0.13 mole), 15.2 g of orthoformic acid trimethyl ester (0.14 mole), 16 ml of anhydrous methanol and 0.3 g of ammonium chloride are mixed and the mixture refluxed for 3 hours. After cooling the ammonium chloride is filtered off and the low boiling products evaporated in vacuum. The residue is taken up in ether, washed twice with water and dried with solid potassium carbonate. The ether is distilled from a water-bath and the residue distilled further through a 5 cm column packed with glass helices. After a fore-run (1.0 g, b. p.<sub>13</sub> = 93°–97°,  $n_D^{25}$  = 1.4522) the main fraction distils at 97°–99°/13 mm. Yield 19.5 g = 82% of a pale-yellow liquid;  $n_D^{25}$  = 1.4519.



Calc. OCH<sub>3</sub> 33.7 Found OCH<sub>3</sub> 33.1

Another distillation through the same column gives 16.7 g = 70 %; pale-yellow liquid, b. p.<sub>13</sub> = 97°–99°;  $n_D^{25}$  = 1.4524.



Calc. C 65.2 H 8.8 OCH<sub>3</sub> 33.7

Found » 64.9 » 9.0 » 33.4

*4-Isopropyl-2-furoic acid (II)*. 20.5 g of isopropylfuraldehyde (0.15 mole) in 30 ml of ethanol is poured into a suspension of silver oxide (from 57.0 g of silver nitrate (0.33 mole)) in 150 ml of 50 % ethanol. A solution of 12.2 g of sodium hydroxide (0.30 mole) in 60 ml of water is added dropwise to the stirred suspension during 15 minutes. The temperature is kept at 40°–45° by cooling. Stirring is continued for 30 minutes without cooling whereby the temperature drops to 33°. Finally the mixture is refluxed for 20 minutes. After filtration the ethanol and part of the water are evaporated in vacuum. The residue is washed once with ether, acidified with concentrated hydrochloric acid and extracted 3 times with ether. The ethereal extract is washed once with water and dried with sodium sulfate. The ether is evaporated in vacuum. Yield 21.0 g of isopropylfuroic acid = 91 %. 1.00 g of the above product was crystallized from ether-petroleum ether and dried (sulfuric acid, 0.1 mm, 20°, 8 hours). Yield 0.84 g; m. p. 76.0°–77.5° (Hershberg apparatus, corr.); Gilman and Calloway<sup>1</sup> found 76°–77°. C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> (154.2) Found neut.equiv. (phenolphthalein indicator) 154.4.

*4-Isopropyl-2-furoic acid methyl ester (V)*. 16.5 g of isopropylfuroic acid, 100 ml of methanol and 9 ml of concentrated sulfuric acid are mixed and refluxed for 4 hours and the ester isolated in the usual manner. The final product is distilled through a 5 cm column packed with glass helices. Yield 13.1 g of isopropylfuroic acid methyl ester = 73 %; colourless liquid, b. p.<sub>14</sub> = 110°–112°;  $n_D^{25}$  = 1.4783.



Calc. C 64.3 H 7.2 OCH<sub>3</sub> 18.5

Found » 64.1 » 7.1 » 17.7

*3-Isopropylfuran (III)*. Six 5.0 g-portions of isopropylfuroic acid are decarboxylated as described by Gilman, Calloway and Burtner<sup>3</sup> (cf. also Shephard, Winslow and Johnson<sup>4</sup>). The distillate from the decarboxylation (21 g) is dried with magnesium sulfate and distilled under nitrogen through a 5 cm column packed with glass helices. Yield 16.6 g of isopropylfuran = 78 %; colourless liquid, b. p.<sub>760</sub> = 111°–113°;  $n_D^{25}$  = 1.4344;  $n_D^{20}$  = 1.4368. Gilman, Calloway and Burtner<sup>3</sup>

obtained a 56 % yield of their product (b.  $p_{760} = 111^\circ - 112^\circ$ ,  $n_D^{20} = 1.4369$ ).

1. Gilman, H., and Calloway, N. O. *J. Am. Chem. Soc.* **55** (1933) 4197.
2. Gilman, H., McCoreckle, M., and Calloway, N. O. *J. Am. Chem. Soc.* **56** (1934) 745.
3. Gilman, H., Calloway, N. O., and Burtner, R. R. *J. Am. Chem. Soc.* **57** (1935) 906.
4. Shephard, A. F., Winslow, N. R., and Johnson, J. R. *J. Am. Chem. Soc.* **52** (1930) 2083.

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## Melting Points of *p*-Nitrobenzyl Esters of Aryl Substituted Propionic Acids

GUST-AD. HOLMBERG

*Institute of Organic Chemistry, Abo Akademi, Abo, Finland*

In connection with other work in progress in this laboratory, a convenient method for identifying carboxylic acids was required. The melting points of the *p*-nitrobenzyl esters prepared according to the

method originally proposed by Reid<sup>1</sup> was found to be suitable for this purpose. The method was first applied to acids with similar constitutions and melting points that had been prepared in this laboratory<sup>2</sup>. As the melting points of these *p*-nitrobenzyl esters may have a general interest in connection with the appraisalment of Reid's method, they are reproduced in Table 1.

The melting points of the *p*-nitrobenzyl esters are rather evenly spread over a temperature range of 55° and almost all differences between the melting points of the derivatives are sufficiently large for identification purposes.

The esters were prepared according to Wild<sup>3</sup>.

1. Reid, E. E. *J. Am. Chem. Soc.* **39** (1917) 124; Lyman, J. A. and Reid, E. E. *ibid.* **39** (1917) 701; Lyons, E. and Reid, E. E. *ibid.* **39** (1917) 1727; Bliche, F. F. and Smith, F. D. *ibid.* **51** (1929) 1947.
2. Holmberg, G. A. *Acta Acad. Aboensis, Math. et Phys.* **XVI** (1949) no. 6; *Acta Acad. Aboensis, Math. et Phys.* **XVII** (1950) no. 1.
3. Wild, F. *Characterisation of Organic Compounds* (1948) 144. Cambridge, Cambridge University Press.

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Table 1.

Propionic acid		<i>p</i> -Nitrobenzyl ester		
Substituents	M.p. °C	M.p. °C	Calc. N	Found N
$\beta, \beta, \beta$ -Triphenyl-	177-178	133-134	3.20	3.26
$\beta, \beta$ -Diphenyl- $\beta$ - <i>o</i> -tolyl-	174.5-175.5	110-111	3.10	3.09
$\beta, \beta$ -Diphenyl- $\beta$ - <i>m</i> -tolyl-	118-119	106-107	3.10	3.11
$\beta, \beta$ -Diphenyl- $\beta$ - <i>p</i> -tolyl-	195-196	120-121	3.10	3.12
$\beta, \beta$ -Diphenyl- $\beta$ - <i>o</i> -anisyl-	169-170	115-116	3.00	2.99
$\beta, \beta$ -Diphenyl- $\beta$ - <i>p</i> -anisyl-	155-156	83-84	3.00	2.99
$\beta, \beta$ -Diphenyl-	154-155	90-91	3.88	3.87
$\beta$ -Phenyl- $\beta$ - <i>o</i> -tolyl-	131-132	83-84	3.73	3.68
$\beta$ -Phenyl- $\beta$ - <i>p</i> -tolyl-	145-146	78-79	3.73	3.77
$\beta$ -Phenyl- $\beta$ - <i>p</i> -anisyl-	124-125	87-88	3.58	3.48
$\beta, \beta$ -Di- <i>p</i> -anisyl-	139-141	93-94	3.32	3.29
$\beta$ -Phenyl- $\beta$ - <i>p</i> -biphenyl-	176-177	110-111	3.20	3.27
$\beta$ -Phenyl- $\beta$ -naphthyl-1-	149-150	104-105	3.40	3.30