

## NOTES

## Bromophenacyl Esters of Organic Acids

BY HAKON LUND AND TAGE LANGVAD

*p*-Bromophenacyl bromide has proved to be a useful reagent for the identification of organic acids. It is therefore of some value to know the properties of as large a number of esters as possible. As a contribution to the knowledge of such compounds we have prepared, carefully purified and analyzed a number of *p*-bromophenacyl esters. Usually the esters may be recrystallized from alcohol, but when they are very slightly soluble in this solvent glacial acetic acid is an excellent solvent for recrystallization.

The purified compounds were analyzed by micro-determination of bromine using the method of Pregl except that the bromine in the solution obtained after the combustion was titrated instead of being determined gravimetrically. 0.05 *N* silver nitrate and 0.05 *N* ammonium thiocyanate in microburets were used. The accuracy is about 0.4% and equals that of the gravimetric method, but the titration is much more convenient. If chlorine is present, a correction for dissolved silver chloride has to be applied. When the solution to be titrated is about 50 cc., this correction amounts to 0.027 cc., which is to be added to the volume of silver nitrate used. The solubility of silver chloride is considerably higher in this solution than in pure water. When chlorine is absent it is unnecessary to filter the solution from silver bromide.

The esters of adipic, *m*-nitrocinnamic, and *p*-nitrocinnamic acids are very slightly soluble in alcohol and were therefore recrystallized from glacial acetic acid.

From pyruvic and malonic acids no ester could be obtained.

*p*-BROMOPHENACYL ESTERS(R means *p*-BrC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>)

Acid	Formula of ester	M. p. (corr.), °C.	Bromine, %	
			Calcd.	Found
Tiglic	CH <sub>3</sub> CH=CH(CH <sub>3</sub> )COOR	67.9	26.9	27.0
Adipic	(—CH <sub>2</sub> CH <sub>2</sub> COOR) <sub>2</sub>	152.6	29.6	29.5
Chloroacetic	CH <sub>2</sub> ClCOOR	103.7	(1) <sup>a</sup>	
<i>m</i> -Hydroxybenzoic	HOC <sub>6</sub> H <sub>4</sub> COOR	176.1–176.4	24.4	24.5
<i>p</i> -Hydroxybenzoic	HOC <sub>6</sub> H <sub>4</sub> COOR	191.3–191.7	24.4	24.6
<i>m</i> -Nitrobenzoic	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COOR	135.4	22.0	22.1
<i>o</i> -Chlorobenzoic	ClC <sub>6</sub> H <sub>4</sub> COOR	107.0	(2) <sup>a</sup>	
<i>m</i> -Nitrocinnamic	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCOOR	178.0	20.5	20.4
<i>p</i> -Nitrocinnamic	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH=CHCOOR	191.0	20.5	20.6
<i>o</i> -Methoxycinnamic	CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCOOR	145.0	21.4	21.3
<i>o</i> -Methoxy-allocinnamic	CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH=CHCOOR	97.5	21.4	21.46

<sup>a</sup> The analytical data are best expressed by calculation of the molecular weights based upon the titration results.

	Mol. wt. calcd.	Mol. wt. found
(1)	291.4	294.0
(2)	353.5	351.0

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## 2-Chloro-5-methylfuran and 2-Methyl-5-nitrofuran

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The recent availability<sup>1</sup> of nuclear substituted 2-furfurals and the highly effective Wolff-Kischner<sup>2</sup> reduction for the conversion of an aldehyde to a methyl group combine to facilitate the allocation of substituents in the furan nucleus and so arrive at generalizations on furan nuclear orientation.

2-Chloro-5-methylfuran has been prepared by the hydrazine-sodium ethylate reduction<sup>2</sup> of 5-chloro-2-furfural. It is identical with the compound recently prepared by the decarboxylation of 5-chloro-2-methyl-3-furoic acid.<sup>3a</sup> The 2-chloro-5-methylfuran is of interest in connection with the rearrangement reactions of 2-furfuryl chloride,<sup>3</sup> particularly as they apply to rearrangements of organometallic compounds. The exclusion of the possibility of a dynamic isomerism of 2-chloro-5-methylfuran with 2-furfuryl chloride<sup>3a</sup> has been confirmed by us. There is an extraordinary difference in reactivity between a nuclear halogen furan like 3-iodofuran and a lateral halogen furan like furfuryl chloride. Studies with metals, leading to the formation of organometallic compounds, indicate that the former compound probably has the most inert iodine attached to a doubly bonded carbon, whereas the latter appears to have the most active chlorine attached to a carbon.<sup>4</sup> The exalted activity of chlorine in 2-furfuryl chloride is attributed by one of us (H. G.) to super-aromatic properties of the furan nucleus. Furfuryl fluoride should form a Grignard reagent with moderate ease, and this RMgF compound should undergo transformations of the kind shown by organometallic compounds containing magnesium, lithium, sodium, etc., when treated with reagents like formaldehyde and ethyl chlorocarbonate. In this connection, F. Breuer has

<sup>1</sup> Gilman and Wright, *Rec. trav. chim.*, **50**, 833 (1931) (for 5-chloro-2-furfural); *THIS JOURNAL*, **52**, 2550, 4165 (1930) (for 5-nitro-2-furfural); *ibid.*, **52**, 1170 (1930), (for 5-bromo-2-furfural).

<sup>2</sup> Wolff, *Ann.*, **394**, 86 (1912); Kischner, *J. Russ. Phys.-Chem. Soc.*, **43**, 1563 (1912); [*Chem. Abstracts*, **6**, 1430 (1912)].

<sup>3</sup> (a) Scott and Johnson, *THIS JOURNAL*, **54**, 2549 (1932); Reichstein, *Ber.*, **63**, 749 (1930); Runde, Scott and Johnson, *THIS JOURNAL*, **52**, 1284 (1930); Reichstein and Zschokke, *Helv. Chim. Acta*, **15**, 249 (1932).

<sup>4</sup> Direct measurements with potassium iodide show that the chlorine in furfuryl chloride is distinctly more active than that in benzyl chloride.