

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*-BrC₆H₄COCH₂)

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

^a 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 availability¹ of nuclear substituted 2-furfurals and the highly effective Wolff-Kischner² 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 reduction² of 5-chloro-2-furfural. It is identical with the compound recently prepared by the decarboxylation of 5-chloro-2-methyl-3-furoic acid.^{3a} The 2-chloro-5-methylfuran is of interest in connection with the rearrangement reactions of 2-furfuryl chloride,³ 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^{3a} 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.⁴ 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

¹ 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).

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

³ (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).

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

shown that 2-methylfuran reacts with ethylsodium or phenylsodium to give a furan-sodium compound which on carbonation yields 5-methyl-2-furoic acid. By analogy with a related reaction with toluene and the xylenes, it is possible that furfurylsodium is first formed and then undergoes a transformation like that observed in the reaction between furfuryl chloride and sodium cyanide.

2-Methyl-5-nitrofuran has been prepared by the Wolff-Kischner² reduction of 5-nitro-2-furfural. It is identical with the methylnitrofuran prepared both by the nitration of 2-methylfuran and the nitration with accompanying decarboxylation of 5-methyl-2-furoic acid.⁵ The identity of these methylnitrofurans has a two-fold significance from the viewpoint of orientation in the furan nucleus. First, it definitely establishes that an α - or 2-substituted furan, irrespective as to whether it is an ortho-para or meta orienting group in benzene types, orients to the other α - or the 5-position. This is evident when one recalls that the nitrofuroic acid obtained by nitration of furoic acid is identical with that obtained by the oxidation of the nitro-2-furfural resulting from the nitration of furfural. Second, the formation of 2-methyl-5-nitrofuran by the nitration of 2-methyl-5-furoic acid proves that the nitro group has taken the position originally occupied by the carboxyl group. This is of importance in the proof of structure of furan compounds because of the uncommon ease of decarboxylation of furoic acids and the accompanying possibility that the 5-methyl-2-furoic acid might have first nitrated and then lost carbon dioxide to give a methylnitrofuran having the nitro group in a position other than that occupied initially by the carboxyl group.

Although the position of the methyl group in 2-methyl-5-nitrofuran is known, it must be admitted that there is no unequivocal evidence for the position of the nitro group. This we are establishing, among several methods, by blocking the β -positions and by the synthesis of 3-nitrofuran, which from our present knowledge of β -substituted furans should give a relatively stable and diazotizable 3-aminofuran.

Experimental

To a solution of 65 g. (0.5 mole) of 5-chloro-2-furfural in 250 cc. of methyl alcohol, chilled in an ice-bath, was added at once 48 g. (0.96 mole) of hydrazine hydrate. After one hour, 56 g. (1 mole) of potassium hydroxide in pellet form was added without agitation, and at the end of twelve hours (spontaneous evolution of nitrogen having ceased) the mixture was distilled from the alkali. In working up the product in a customary manner there was obtained 21 g. or a 36.2% yield of 2-chloro-5-methylfuran: b. p. 110°, n_D^{20} 1.4619, d_4^{20} 1.180.

Anal. Calcd. for C_6H_6OCl : Cl, 30.44. Found: Cl, 30.66.

In accordance with other observations,^{3a} the compound is relatively stable and after several months' standing in a refrigerator (without the addition of a stabilizer like

⁵ Rinkes, *Rec. trav. chim.*, **49**, 1118 (1930).

hydroquinone) showed only slight decomposition. It does not react in ether with ordinary or activated magnesium. A vigorous reaction takes place with sodium, and this is being investigated. From other studies it appears that alkyl groups labilize furan nuclear halides as, for example, the β -iodine in 2,5-dimethyl-3-iodofuran.

In the reduction of 5-nitro-2-furfural, copper bronze in quinoline in place of potassium hydroxide was used for the decomposition of the hydrazone. The 2-methyl-5-nitrofuran was shown to be identical, by the method of mixed melting points, with an authentic specimen.⁵ The copper bronze-quinoline procedure for removal of nitrogen is novel, we believe, and its application was indicated because of the marked sensitivity of α -nitrofurans to strong alkalies.

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Phenanthrene-1-carboxylic Acid

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Following the request of Dr. E. Mosettig for a sample of the above substance with which to compare an isomer isolated in the Virginia Laboratory,¹ this new phenanthrene derivative was prepared from the 1-sulfonic acid,² a small sample of which was still available.

Phenanthrene-1-nitrile, prepared from 1 g. of potassium phenanthrene-1-sulfonate and 2 g. of potassium ferrocyanide, was obtained in a pure condition (yield 0.4 g.) by distillation *in vacuo* and crystallization from alcohol. It formed stout, colorless needles melting at 128°.

Anal. Calcd. for $C_{15}H_9N$: C, 88.64; H, 4.47. Found: C, 88.50; H, 4.58.

Phenanthrenequinone-1-nitrile resulted from the oxidation of the phenanthrene derivative with chromic acid at 90°. It is sparingly soluble in glacial acetic acid and separates as fine, orange needles melting at 339°.

Anal. Calcd. for $C_{15}H_7O_2N$: C, 77.24; H, 3.03. Found: C, 77.30; H, 3.25.

Phenanthrene-1-carboxylic acid amide was obtained by boiling the corresponding nitrile with alcoholic alkali for two hours. It formed colorless plates, m. p. 284°, from dilute acetic acid.

Anal. Calcd. for $C_{15}H_{11}ON$: C, 81.41; H, 5.01. Found: C, 81.50; H, 5.26.

Phenanthrene-1-carboxylic Acid.—The amide is hydrolyzed only with difficulty. The reaction with alcoholic alkali was not complete even after heating for several hours at 160°. The acid is readily soluble in alcohol or benzene and crystallizes well from the former solvent as colorless needles melting at 232–233°.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: C, 81.22; H, 4.56.

The methyl ester, prepared with diazomethane, is very readily soluble even in cold organic solvents. Purified by distillation, it melted at 57°.

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¹ Mosettig and van de Kamp, *THIS JOURNAL*, 54, 3328 (1932).

² Fieser, *ibid.*, 51, 2460 (1929).