METHOXYL DETERMINATIONS ON ALKYL ESTERS OF 2-METHOXYBENZOIC ACID*

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In the course of another investigation it became desirable to ascertain to what extent certain alkyl ester groups would interfere with methoxyl determinations made on derivatives of methoxy-aromatic acids.

The Zeisel method in its various modifications has long been used, on both macro and micro scale, for the determination of methoxyl and ethoxyl groups; with certain changes in apparatus and technic, it has been recommended for propoxyl and butoxyl determinations[1]. It might be inferred, therefore, that a methoxyl determination by the usual procedure could be carried out without interference by pentoxyl groups. That this is not the case is shown here.

The ready availability of salicylic acid made it convenient to use as a starting material for the preparation of suitable test compounds. This paper reports the preparation and properties of the n-propyl, n-butyl, and n-pentyl esters of 2-methoxy benzoic acid, and results of methoxyl determinations made upon them by the micro Zeisel method.

Of the simple alkyl esters of 2-methoxybenzoic acid, only the methyl[2] and ethyl[3] esters have been described in the literature.

EXPERIMENTAL

2-Methoxybenzoic acid. This compound was prepared by methylating salicylic acid with dimethyl sulfate and purifying the product according to the method of Graebe[4]. One mole (138 g.) of salicylic acid yielded 95.3 g. of 2-methoxybenzoic acid (62.7% of theoretical); recovery of salicylic acid was 32.8 g., making the yield of desired product 81.8% based on salicylic acid actually used. The melting point was 101.5-103.5°C. after recrystallization from water.

Esters of 2-methoxybenzoic acid. As typical of the method used, the preparation of n-butyl 2-methoxybenzoate is described here. The procedure was essentially that used by Cavill and Gibson[5] for making n-butyl 4-methoxybenzoate. A solution of 30.4 g. (0.2 mole) of 2-methoxybenzoic acid in 100 ml. of n-butanol and 100 ml. of toluene was treated with 10 drops of concentrattrated sulfuric acid, and refluxed until no more water accumulated in the graduated trap which was interposed between the flask and the condenser. In about three hours 4 ml. of water were caught (theoretical 0.2 mole = 3.6 ml.). The reaction mixture was cooled, washed with water, sodium carbonate solution, water, dried over anhydrous sodium

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[1] See, for example, Sidney Siggia, "Quantitative Organic Analysis via Functional Groups," p. 30, John Wiley and Sons, Inc., 1949.

[2] See Beilstein, "Handbuch der Organischen Chemie," 4th Edition, Vol. X, p. 71; 1st Supplement X, p. 32.

[3] Ibid Vol. X, p. 74; 1st Supplement X, p. 34.

[4] Ann. *340*, 210; *139*, 137; cf. Beilstein X. p. 64.

[5] G. W. K. Cavill and N. A. Gibson, J. Soc. Chem. Ind. *66*, 274, 1947.

TABLE I.—METHOXYL DATA FOR 1, 2-C_6H_4 (COOR) (OCH_3).

R	Theoret. OCH_3	—OR found (as —OCH_3)	Flushing time (Minutes)	Number of alkoxyl groups
n-C_3H_7	15.98	30.16	45*	1.89
n-C_4H_9	14.90	28.28	45*	1.90
n-C_5H_{11}	13.96	17.64	20	1.26
n-C_5H_{11}	"	26.72	80	1.91
n-C_5H_{11}	"	27.16	90	1.95

* Approximate.

sulfate, the butanol and toluene distilled off, and the product distilled at diminished pressure. The yield was 38.3 g. or 92% of the theoretical. This was redistilled through a short column prior to analysis. Boiling point, 112°C. at 1.2 mm.; f.p., —23° to —25°; n_D^{20}, 1.51125; d_4^{20}, 1.062. Analysis: Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.22; H, 7.68.

The n-pentyl ester, prepared in a similar manner from 15. 2 g. (0.1 mole) of 2-methoxybenzoic acid, 25 g. of pentanol-1, 75 ml. of toluene and 3 drops of sulfuric acid, was isolated in 69% yield. B.p., 112-13° at 0.8 mm.; n_D^{20}, 1.50668; d_4^{20}, 1.045. Anal.: Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.03; H, 8.19.

In the preparation of the propyl ester, 150 ml. of benzene were used in place of toluene, with 30.4 g. of the acid, 60 ml. of propanol and 2 ml. of sulfuric acid. The crude ester, 37.1 g. or 95.6% of theoretical, required several redistillations before it was sufficiently pure for analysis. B.p., 114.8-115.5° at 1.5 mm.; n_D^{20}, 1.51566; d_4^{20}, 1.085. Anal.: Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.88, 68.10; H, 7.44, 7.44.

A small sample of each of the esters was saponified and the 3, 5-dinitrobenzoate was prepared from the alcohol formed. The derivatives thus produced were those of the normal alcohol proving that no rearrangement of the alkyl groups had occurred during esterification.

Methoxyl determinations were run essentially as described by Pregl[6], with variations in the length of the flushing period. Table I gives the results of these determinations, and shows the effect of varying the fushing period in the case of the pentyl ester.

It is thus shown that even with the normal 20-minute flushing period, the presence of n-pentyl ester groups results in a high value for methoxyl, and that with longer flushing periods, both ether and ester alkoxyl groups in these compounds can be determined with a fair degree of completeness.

SUMMARY

Three new compounds have been described and their physical constants reported. These are the n-propyl, n-butyl, and n-pentyl esters of 2-methoxybenzoic acid.

In all cases the alkoxyl groups present as esters have been split off with hydriodic acid, and the resulting alkyl iodides have distilled over along with methyl iodide from the ether group in the micro Zeisel methoxyl procedure.

[6] Pregl-Grant, "Quantitative Organic Analysis," p. 146, The Blakiston Co., 1946.