a crude solid was obtained, from which only 3.8 g. of pure base, m. p. 84–85°, was obtained; yield, 44%.

Hydrochloride of Ethyl 4-Hydroxymethyl-3-aminobenzoate.—Dry hydrogen chloride was passed into an ether solution of the amino ester. The resulting precipitate was recrystallized from a mixture of absolute alcohol and petroleum ether. When pure, the hydrochloride melts with decomposition at 129–130°. It is soluble in water. Very little pure product could be obtained, due to formation of resin, probably caused by a condensing action of hydrogen chloride on the alcohol and amino groups present.

Anal. Calcd. for $C_{10}H_{14}O_3NCl$: Cl, 15.32. Found: 15.71.

***n*-Butyl 4-Hydroxymethyl-3-nitrobenzoate,** $C_6H_3(HOCH_2)(NO_2)(COOC_4H_9)$.—This was prepared similarly to the corresponding ethyl ester, using absolute butyl alcohol saturated with hydrogen chloride instead of ethyl alcohol. After the reaction was complete, the ammonium chloride was filtered off, the excess of butyl alcohol was removed on the water pump and the residue distilled. The butyl ester distils as a heavy, yellow oil; b. p., 198–203° (3 mm.); yield, 66%.

Anal. Calcd. for $C_{12}H_{15}O_5N$: C, 56.92; H, 5.93. Found: C, 57.02; H, 5.73.

***n*-Butyl 4-Hydroxymethyl-3-aminobenzoate,** $C_6H_3(HOCH_2)(NH_2)(COOC_4H_9)$.—Ten g. of butyl nitro ester in 500 cc. of 50% alcohol and 5 cc. of concd. hydrochloric acid was reduced by means of colloidal platinum. The platinum was removed as before, the alcohol evaporated by means of the water pump, and the solution made alkaline and extracted with ether. Four g. of product, m. p. 73–74°, was obtained. The pure butyl ester is a white solid, m. p. 76–77°, soluble in dil. hydrochloric acid. Due to resinification, its hydrochloride could not be isolated.

Anal. Calcd. for $C_{12}H_{17}O_3N$: C, 64.57; H, 7.62. Found: C, 64.90; H, 7.30.

Summary

1. Ethyl and butyl 4-hydroxymethyl-3-aminobenzoates have been prepared, thus making available in soluble form the corresponding esters of *p*-hydroxymethyl-benzoic acid intended for use as local anesthetics.

2. A comparison of methods of reduction of ethyl 4-hydroxy-methyl-3-nitrobenzoate has been made.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, NO. 34]

ETHYLHEXYLACETIC ACID AND ITS ESTERS

BY ARTHUR W. DOX

RECEIVED JULY 23, 1925 PUBLISHED DECEMBER 12, 1925

The malonic ester synthesis has for many years been used for the preparation of fatty acids of the $C_nH_{2n+1}COOH$ series. The method is so well known and of such wide application that a discussion of the simple reactions involved would be superfluous. The present note merely describes the acid obtained from ethyl ethylhexylmalonate by saponification and expulsion of carbon dioxide, and the esters prepared from the acid by refluxing with methyl, ethyl, propyl and butyl alcohols, respectively, in the presence of a small amount of concd. sulfuric acid.

***dl*-Ethyl-*n*-hexylacetic Acid**, b. p. 252–255°, d_{25} 0.8905, was obtained in nearly quantitative yield by distillation of ethylhexylmalonic acid.[1] It is a colorless, oily liquid, practically insoluble in water, and has a slightly rancid odor.

Anal. Subs., 0.2048: CO_2, 0.5276; H_2O, 0.2169. Calcd. for $C_{10}H_{20}O_2$: C, 69.77; H, 11.63. Found: C, 70.26; H, 11.77.

The properties and analyses of the esters prepared are given in Table I.

TABLE I

ESTERS OF *dl*-ETHYL-*n*-HEXYLACETIC ACID

Ester	Formula	B. p., ° C.	d_{25}	Analysis			
				Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Methyl	$C_{11}H_{22}O_2$	213–215	....	70.97	70.32	11.83	11.89
Ethyl	$C_{12}H_{24}O_2$	221–223	0.8580	72.00	71.80	12.00	12.05
Propyl	$C_{13}H_{26}O_2$	238–240	.8578	72.90	72.80	12.15	12.26
n-Butyl	$C_{14}H_{28}O_2$	255–257	.8571	73.68	73.72	12.28	12.47

Boiling points are corrected.

The methyl and ethyl esters had a faint, fruity odor; the others were practically odorless.

The esters do not readily form amides. Both the methyl and ethyl esters were dissolved in absolute alcohol, cooled to 0° and saturated with dry ammonia. After standing under pressure for two weeks, only the unchanged ester could be recovered, with no evidence of the formation of amide.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE IDENTIFICATION OF PRIMARY ALKYL BROMIDES AND IODIDES

BY C. S. MARVEL, C. G. GAUERKE AND E. L. HILL

RECEIVED JULY 27, 1925 PUBLISHED DECEMBER 12, 1925

In qualitative organic analysis the final test for the identification of any compound is the preparation of some solid derivative of definite melting point. For routine work it is quite essential that this derivative be easily prepared and purified. A large number of general derivatives for classes of compounds are now commonly used, such as the aryl sulfonyl derivatives of amines, the *p*-bromophenacyl and the *p*-bromobenzyl esters of acids. However, no general type of derivative is available for the alkyl halides.

In connection with the preparation of dialkyl mercury compounds from the Grignard reagent and mercuric halides[1] it has been noticed that the alkyl mercuric halides are almost always well crystallizable, sharply melting compounds. It was thought that they should make excellent derivatives for identification of the alkyl halides.

[1] Dox, THIS JOURNAL, **46**, 1709 (1924).

[1] (a) Marvel and Gould, THIS JOURNAL, **44**, 153 (1922). (b) Marvel and Calvery, *ibid.*, **45**, 820 (1923).