***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, % Calcd.	 Found	 Hydrogen, % 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

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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.

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[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).

In actual practice it has been found that this is true only of the primary alkyl bromides and iodides. The method involves the preparation of the Grignard reagent and its treatment with the corresponding mercuric halide. The alkyl chlorides do not always react readily to give the Grignard reagent and as a result the mercury compound is not easily prepared. The primary alkyl bromides and iodides react with magnesium very easily to give the Grignard reagent and this in turn reacts with the corresponding mercuric halide to give good yields of the alkyl mercuric bromide or iodide. The derivatives from the bromides are very easily purified. The iodide derivatives sometimes need several crystallizations from alcohol to remove the mercuric iodide completely.

These derivatives are easily prepared in a test-tube, using small quantities of the reagents. The products have definite melting points that vary enough from one to another to make the derivatives satisfactory for laboratory use. A number of the derivatives have been prepared by other methods and are now described in the literature. The melting points of the common alkyl derivatives are given in Table I.

Table I

Melting Points of Some Alkyl Mercuric Halides

Alkyl group	M. p. of chloride, ° C.	M. p. of bromide, ° C.	M. p. of iodide, ° C.
Methyl	170[a]	160[a]	145[a]
Ethyl	192.5[a]	193.5	182[a]
n-Propyl	140	138	112.5
*iso*Butyl	...	55.5	72
n-Butyl	127.5[b]	129[b]	117
iso-Amyl	86	80	122
n-Amyl	...	122	...
n-Hexyl	...	118.5	...
n-Heptyl	...	114.5	...
n-Octyl	...	109	...

[a] Crymble, *J. Chem. Soc.*, **105**, 668 (1914).

[b] Ref. 1 a, p. 156.

The objection may be raised that the mercuric derivatives are poisonous. This is true, but when reasonable care is used to keep the solutions off the skin the preparation of one of these derivatives is no more dangerous than many operations commonly carried out in the organic chemical laboratory. It is very important to avoid an excess of the Grignard reagent, since this would produce the volatile mercury dialkyl which is always more toxic than the corresponding alkyl mercuric halide.

Experimental Part

Preparation of Alkyl Mercuric Halides.—In general, the derivatives are prepared by allowing not more than 1 cc. of alkyl halide to react with 0.3 g. of magnesium in the presence of about 15 cc. of dry ether. When the reaction is complete the solution is filtered through a little glass wool to remove the excess of magnesium and allowed to flow into a test-tube containing about 4.5–5.0 g. of mercuric bromide or iodide, depending on the halogen in the original alkyl halide. The reaction mixture is warmed and shaken for a few minutes and then evaporated to dryness. The residue is boiled with about 20 cc. of 95% alcohol and the solution is filtered, diluted with 10 cc. of water and cooled. The alkyl mercuric halide separates in beautiful crystals, one crystallization usually giving a sharply melting product.

Runs with greater quantities were also made in order to obtain enough of the various derivatives for determination of melting points and analysis. The new compounds that have been prepared are given in Table II.

Table II

New Alkyl Mercuric Halides

	M. p., ° C. (corr.)	Analysis		
Mercuric bromide		Formula	Calcd., %	Found, %
Ethyl	193.5	C_2H_5HgBr	C, 7.76	7.72
n-Propyl	138	C_3H_7HgBr	C, 11.12	11.18
*iso*Butyl	55.5	C_4H_9HgBr	Hg, 59.46	59.1
n-Amyl	122	$C_5H_{11}HgBr$	Hg, 57.05	56.80
n-Hexyl	118.5	$C_6H_{13}HgBr$	Hg, 54.86	54.36
n-Heptyl	114.5	$C_7H_{15}HgBr$	Hg, 52.58	52.21
n-Octyl	109	$C_8H_{17}HgBr$	Hg, 50.96	50.72
Mercuric iodide				
n-Propyl	112.5	C_3H_7HgI	C, 9.72	9.69
n-Butyl	117	C_4H_9HgI	C, 12.48	12.59
*iso*Butyl	72	C_4H_9HgI	C, 12.48	Not analyzed

Summary

Primary alkyl bromides and iodides are easily converted into the corresponding mercuric halides, which are suitable derivatives for identification.

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[Contribution from the Department of Chemistry, Yale University]

NITROGEN TETROXIDE AS A REAGENT FOR DIAZOTIZATION

By Bruce Houston[1] and Treat B. Johnson

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The object of this research, the results of which are recorded in this paper, was to demonstrate experimentally that the diazotization of a primary aromatic amine can be accomplished successfully by allowing the base to interact with pure nitrogen tetroxide, N_2O_4, in an anhydrous solvent at ordinary temperature. This reaction has now been applied

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[1] Constructed from a dissertation presented by Bruce Houston to the Faculty of the Graduate School of Yale University, June, 1923, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.