p-NITROBENZYL HALIDES AS REAGENTS FOR THE IDENTIFICATION OF PRIMARY AND SECONDARY AMINES.*

BY EDWARD LYONS.

The *p*-nitrobenzyl halides[1] have been found to be excellent reagents for the identification of a large number of acids, phenols and alcohols.[2] Lyons and Dox[3] have used the chloride for the preparation of a number of derivatives of the barbituric acid series. The reagent, *p*-nitrobenzyl chloride, has been found to be unsuitable for the identification of tertiary amines.[4] With primary and secondary amines, however, there is, usually, reaction with formation of colored crystalline derivatives of convenient solubilities and melting points. Alkyl amines have given pale yellow derivatives. In the aromatic series, monoamines have given deeper yellow substances, while the diamines have yielded brick-red derivatives.

PROCEDURE.

The procedure is essentially the same as that used for the identification of acids.[3] Working with known amines, the proportions used are based on the equation

$$RNH_2 + 2XCH_2C_6H_4NO_2 + Na_2CO_3 \longrightarrow RN(CH_2C_6H_4NO_2)_2$$

for primary amines, and

$$R_2NH + XCH_2C_6H_4NO_2 + {}^1/_2Na_2CO_3 \longrightarrow R_2NCH_2C_6H_4NO_2$$

for secondary amines.

With unknowns, based on the averages obtained from those amines which are recorded below, the proportions are roughly as follows:

For primary amines, 0.5 Gm. amine : 1.5 Gm. reagent : 0.4 Gm. Na_2CO_3
For secondary amines, 0.5 Gm. amine : 0.75 Gm. reagent : 0.2 Gm. Na_2CO_3
For diamines, 0.5 Gm. amine : 2.5 Gm. reagent : 0.8 Gm. Na_2CO_3

(Reagent = *p*-nitrobenzyl chloride.)

The amine and reagent are dissolved in a flask, in 10–20 cc. 95 per cent alcohol, and the carbonate dissolved in 5–10 cc. water is then added. Usually, a clear solution is obtained. Should some carbonate be precipitated it may be disregarded. The mixture is refluxed during one hour. If the derivative formed is insoluble it is filtered, washed with acidulated water, then with water, and in some cases with alcohol and ether. If no precipitation occurs, even on cooling, hot water is added to the reaction mixture till a turbidity persists. On cooling, the derivative usually precipitates. It is recrystallized from a suitable solvent. Usually two crystallizations are enough to give a constant melting substance. The yields are very good—50 per cent of theory, or better. No attempt was made to recover all fractions since high purity rather than quantity was desired. To avoid mixtures, when

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[1] In this work the bromide and chloride were used.

[2] Reid, *et al.*, *J. A. C. S.*, 39 (1917), 124, 304, 704, 1249, 1727.

[3] Lyons and Dox, *Ibid.*, 51 (1929), 288.

[4] Marvel, Scott and Amstutz, *Ibid.*, 51 (1929), 3638.

working with primary amines, the aim was to get a completely substituted amine. In Table I are given the derivatives prepared, with their several characterizations.

TABLE I.—*p*-NITROBENZYL DERIVATIVES OF.

Amine.	Composition, R = $-CH_2C_6H_4NO_2$.	M. p.* ° C.	Color.	Solubilities.
Methylamine[1]	$Me.NR_2$	102	light yellow	v. s. C_6H_6, Me_2CO, Et_2O, less in EtOH
Ethylamine[2]	$Et.NR_2$	67	light yellow	s. EtOH, pet. Et_2O
Ethyl-aminoacetate	$Et.CO_2.CH_2.NR_2$	108	light yellow	v. s. EtOH, Et_2O
Benzylamine	$C_6H_4CH_2.NR_2$	144	light yellow	s. EtOH, C_6H_6, insol. pet. Et_2O
Ethyl-*p*-aminobenzoate	$Et.CO_2C_6H_4NR_2$	117	canary yellow	s. EtOH, Et_2O, C_6H_6
Propyl-*p*-aminobenzoate	$Pr.CO_2C_6H_4NR_2$	114	canary yellow	v. s. EtOH, Et_2O, C_8H_6
p-Aminobenzene-sulphonic acid (sulphanilic acid)	$HSO_3C_6H_4-NR_2$	chars	canary yellow	s. s. organic solvents; sol. in alk.
Aniline[2a]	$C_6H_5.NR_2$	168	deeper yellow	s. s. EtOH, Et_2O; v. s. C_6H_6
Ethylaniline	$C_6H_5.NEt.R$	67	deeper yellow	v. s. EtOH, Et_2O, C_6H_6
Phenylaniline (Diphenylamine)	$(C_6H_5)_2.NR$	96	deeper yellow	s. EtOH, Et_2O, C_6H_6
p-Aminodimethylaniline	$Me_2NC_6H_4.NR_2$	210	brick red	v. s. C_6H_6, Me_2CO
o-Phenylenediamine	$R_2N.C_6H_4.NR_2$	198	brick red	s. EtOH, C_6H_6, AcOH
p-Phenylenediamine	$R_2N.C_6H_4.NR_2$	225	brick red	s. EtOH, less in C_6H_6 and Et_2O
Benzidine	$R_2N.C_6H_4-C_6H_4NR_2$	228	brick red	s. s. in organic solvents

* Uncorrected.

[1] Strakosch, *Ber.*, 6 (1873), 1062. Sealed tube reaction, m. p. 104° C.

[2] Paal and Spranger, *Ber.*, 30 (1897), 64. Sealed tube reaction.

[2a] As by-product in making the mono-*p*-nitrobenzyl derivative.[2]

SUMMARY.

p-Nitrobenzyl halides are useful reagents for the identification of primary and secondary amines. Alkyl amines yield light yellow derivatives, aromatic monoamines give deeper yellow bodies while the diamines yield brick-red derivatives. In general they possess definite melting points and differ in solubility from the mother substance thus adding to the ease of purification.

A TOXICOLOGICAL INVESTIGATION OF MERCURY AND LEAD.*

BY L. W. RISING AND E. V. LYNN.

Because of the numerous deaths attributable to mercury and lead and the subsequent seeking of chemical evidence, it would be well to have available certain experimental data which would indicate: The effect of preservatives or putrefaction on the recoverable amount of these substances, and how long after death an analyst might reasonably expect to find the full quantity of drug which was present in the body at the time of the demise. There is always the possibility of unsuspected organic combinations which might render an unknown quantity of either chemical proof against the present procedures for their isolation and determination.

In order to secure these quantitative data, a series of specimens consisting of lead or mercury in contact with organic material both with and without added preservatives was made up. The series was sufficiently large in number so that the poisons were exposed to nearly all of the conditions which they might encounter if the bodies containing them were embalmed, exposed to the natural action of putrefaction, or the organs removed for analysis and preserved with the usual tissue preservatives.

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* Scientific Section, A. PH. A., Miami meeting, 1931.