

the reactivity of bromine water is due to nascent bromine, and a mechanism for the addition of halogens to double bonds has been proposed.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

### 3-NITROPHTHALIC ANHYDRIDE AS A REAGENT FOR ALCOHOLS

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The reagent most commonly recommended for the identification of the lower monohydric alcohols is 3,5-dinitrobenzoyl chloride.<sup>2</sup> It is common practice to prepare a fresh sample of this chloride for each test, making its use somewhat unpleasant and tedious. The present paper reports a study of the use for identification of such alcohols of 3-nitrophthalic anhydride. This substance is easily prepared and keeps well. It readily gives crystalline derivatives of definite melting point with the alcohols in question, and these have solubilities that make hot water a suitable solvent for recrystallizing small quantities, thus avoiding any question of the possibility of alkyl interchange with the solvent. Furthermore, the mono-esters thus obtained still have one free carboxyl group, so that the equivalent weight of unknown alkyl radicals can readily be determined by titration.

3-Nitrophthalic acid was prepared by the method of Miller.<sup>3</sup> Nitric acid, d. 1.45, was as effective as that of d. 1.50, and caused less fuming. The yield was uniformly 28-30%, as also reported by Cohen, Woodroffe and Anderson.<sup>4</sup> The anhydride was readily made by heating the acid with acetic anhydride.<sup>5</sup>

The mono-esters were best prepared by treating the anhydride with about half its weight of the alcohol, and heating on a water-bath for five to ten minutes after the mixture became liquid. The products were then dissolved in hot water and allowed to crystallize. One or two recrystallizations usually gave products of constant melting points. The substances so obtained are 2-mono-alkyl esters of 3-nitrophthalic acid (I).<sup>6</sup> McKen-

<sup>1</sup> The material here presented was used by Jacob Sacks in partial fulfillment of the requirements for the degree of Master of Science in the University of Chicago.

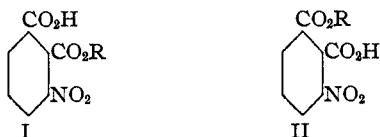
<sup>2</sup> (a) Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, 1904, vol. 1, p. 168. (b) Kamm, "Qualitative Organic Analysis," John Wiley and Sons, 1923, p. 150.

<sup>3</sup> Miller, *Ann.*, 208, 233 (1881). E. R. Littman [THIS JOURNAL, 47, 1980 (1925)] has since published what appears to be a much improved method for the preparation of this acid.

<sup>4</sup> (a) Cohen, Woodroffe and Anderson, *J. Chem. Soc.*, 109, 233 (1916). (b) Miller's statement that the yield is 40% apparently refers to percentage by weight of original phthalic anhydride.

<sup>5</sup> McKenzie, *J. Chem. Soc.*, 79, 1157 (1901).

<sup>6</sup> (a) Wegscheider and Lipschitz, *Monatsh.*, 21, 787 (1900). (b) Marckwald and McKenzie, *Ber.*, 34, 486 (1901).



zie<sup>6</sup> has shown that small amounts of the isomeric esters (II) are formed but if this is so they are eliminated in the purification process.

The aliphatic esters of this type (I) previously described were prepared, and their solubilities in water at 20° determined, with the results listed in Table I. The *isopropyl* and *n*-butyl esters are new. The melting points given are those found in this work, and could be reproduced without difficulty. Except as indicated, they agreed with those given in Ref. 4 a, p. 223. Somewhat lower values have been reported in some cases by earlier workers.

From 2 drops of 95% ethyl alcohol and 0.2 g. of the anhydride, enough of the ester for half a dozen determinations of the melting point was easily obtained, and similar results could be obtained with other pure alcohols. The reagent reacts, however, with water at least as rapidly as with alcohol, so that when 50% ethyl alcohol was used, mixtures resulted which, as titration showed, contained only 29–36% of the desired ester, mixed with nitrophthalic acid. Separation of such mixtures is not to be recommended. Accordingly, in the case of relatively dilute alcoholic solutions, potassium carbonate was added in excess to salt out the alcohol, and the alcohol layer pipetted off for testing. By this procedure, satisfactory results were obtained with as little as 2 cc. of a 10% alcoholic solution.

TABLE I  
SOLUBILITY AT 20°

2-Mono-ester	M. p. °C.	Soly. (G. per 100 g. of H <sub>2</sub> O)	2-Mono-ester	M. p. °C.	Soly. (G. per 100 g. of H <sub>2</sub> O)
Methyl (monohydrate)	below 100	0.200	<i>n</i> -Butyl <sup>d</sup>	146–7	0.051
Methyl (anhydr.) <sup>a</sup>	152–3	.185	<i>iso</i> Butyl	182–3 <sup>e</sup>	.024
Ethyl	156–7	.290	<i>iso</i> -Amyl	165–6	.024
<i>n</i> -Propyl	141–2 <sup>b</sup>	.114	act. Amyl	157–8	..
<i>iso</i> Propyl <sup>c</sup>	152–3	.082			

<sup>a</sup> Water solutions of the methyl ester always gave the hydrate on cooling. It loses its water rapidly at 100°.

<sup>b</sup> Ref. 4 a, p. 223, gives 138–9°.

<sup>c</sup> Not previously described. Mol. wt. (by titration with alkali). Calcd. for C<sub>11</sub>H<sub>11</sub>O<sub>6</sub>N: 253. Found: 253, 255.

<sup>d</sup> Not previously described. Mol. wt. (by titration with alkali). Calcd. for C<sub>12</sub>-H<sub>13</sub>O<sub>6</sub>N: 267. Found: 267, 267.

<sup>e</sup> Ref. 4 a, p. 223, gives 176–7°.

The solubilities indicated show sufficiently what small losses are to be expected in the purification of these substances. The melting points do not show as large a variation for the various esters as would be desirable. Even in the case of the dinitrobenzoates, however, it is usually recommended

that parallel experiments be made with known alcohols, so that the identity of the esters obtained may be confirmed by the determination of the melting points of mixtures. Special tests have shown that all the pairs of mono-alkyl nitrophthalates listed which have melting points sufficiently near to one another to be readily confused, form mixtures with much lower melting points. It is accordingly believed that 3-nitrophthalic anhydride may be found generally useful for the identification of the simpler alcohols.

### Summary

The use of 3-nitrophthalic anhydride as a reagent for the qualitative identification of alcohols has been studied. The results reported seem to justify a recommendation for the use of the procedure outlined.

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## STUDIES IN VAPOR PRESSURE. I. THE NITRO-ANILINES

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The vapor pressures and boiling points of numerous organic compounds have been determined by methods that have, in many cases, proved unreliable. The physical constants of a very large number of these compounds, particularly the intermediates used in the manufacture of dyes, have never been determined. As a result of these conditions the National Research Council has requested that the vapor pressures and boiling points of these compounds be determined by the more accurate methods that are in use at the present time.

This paper reports a study of the vapor pressures of the three isomeric nitro-anilines and gives their latent heats of vaporization and entropies.

A comprehensive study of the vapor pressures of the more important organic compounds that enter into the manufacture of dyes is being undertaken, and the results of these studies will appear in subsequent publications.

The method used for the measurements here recorded was devised by Smith and Menzies.<sup>1</sup> This method has been used in the accurate determination of the vapor pressures of a number of organic compounds, among which may be mentioned phthalic anhydride,<sup>2</sup> naphthalene, anthracene, phenanthrene, anthraquinone,<sup>3</sup> carbazole<sup>4</sup> and the mono- and dimethyl- and -ethylanilines.<sup>5</sup>

<sup>1</sup> Smith and Menzies, *THIS JOURNAL*, **32**, 1416 (1910).

<sup>2</sup> Monroe, *J. Ind. Eng. Chem.*, **12**, 969 (1920).

<sup>3</sup> Nelson and Senseman, *ibid.*, **14**, 58 (1922).

<sup>4</sup> Senseman and Nelson, *ibid.*, **15**, 382 (1923).

<sup>5</sup> Nelson and Wales, *THIS JOURNAL*, **47**, 867 (1925).