[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Analytical Procedures Employing Karl Fischer Reagent.
X. The Determination of Aliphatic Hydroxy Amines (Amino Alcohols)[1]

BY DONALD MILTON SMITH, J. MITCHELL, JR., AND WALTER HAWKINS

The acidimetric methods for the determination of alcoholic hydroxyl usually are based on acetylation involving acetyl chloride[2,3] or on some modification of the Verley and Bölsing acetic anhydride procedure.[4] These methods are subject to a marked loss in sensitivity where the sample contains considerable amounts of water or acids. In addition primary and secondary amines interfere, often to a variable extent.

In an earlier publication from this Laboratory[5] an esterification procedure for the determination of alcoholic hydroxyl was described, depending upon the general reaction

$$ROH + CH_3COOH = CH_3COOR + H_2O$$

This technique, employing boron trifluoride as the esterification catalyst, has been extended to include hydroxyamines. As in the previous case the water liberated in the above reaction, which is equivalent to the hydroxyl esterified, is determined by direct titration with Karl Fischer reagent. Since the reaction of the amine group with the acid or boron trifluoride does not involve water, no interference is encountered.

The new procedure is applicable to aliphatic mono- and polyhydric hydroxyamines in general, including branched chain types and such aromatic hydroxyamines as have the hydroxyl group attached to an aliphatic side chain. The method is applicable also to the determination of hydroxyl in the presence of ammonia or amines. Aminophenols, however, do not react completely.

Experimental

Reagents.—The esterification reagent is prepared by dissolving about 200 g. of boron trifluoride gas[6] in sufficient Merck C. P. glacial acetic acid to make one liter of solution. Dry Baker C. P. or Eastman Kodak No. 214-H pyridine may be used without further purification. Karl Fischer reagent is prepared as indicated in an earlier publication.[7]

Analytical Procedure.—The sample, containing up to 0.1 equivalent of hydroxyl, is weighed into a 50-ml. glass-stoppered volumetric flask about one-third filled with glacial acetic acid. (It is usually safer to chill the flask containing the acetic acid before addition of the sample.) The solution is made up to volume with more acetic acid. Five ml. (using calibrated pipet) of the sample solution is transferred to a 250-ml. glass-stoppered volumetric flask[8] and 20 ml. of the esterification reagent added. The flask is stoppered tightly and together with a control containing 20 ml. of reagent and 5 ml. of acetic acid, is placed in a water-bath or oven at 70 ± 2° for two hours. At the end of this time the flasks are removed and allowed to cool to room temperature spontaneously. Ten ml. of dry pyridine is added to each and the mixture titrated with Karl Fischer reagent.

After correction for the water in acetic acid, esterification reagent and pyridine, the millimoles of water present after reaction less the water originally present, are equal to the milliequivalents of free hydroxyl in the sample.

The water originally present may be obtained by titrating 5 ml. of the original acetic acid solution with Fischer reagent. A correction for the water present in the acetic acid is obtained by titrating a 5-ml. portion and correcting to the volume of acid actually present in the sample solution.

Analytical Results

The experimental results obtained with twelve hydroxyamines are given in Table I. With the exception of the mono- and diethanolamines the trade products were used without further purification.

Aminophenols do not esterify completely under the conditions of the general procedure; *m*-aminophenol reacted only about 40%.

The precision and accuracy average about ±0.3%, comparing favorably with the earlier hydroxyl procedure.[5]

TABLE I

ANALYTICAL DATA FOR HYDROXYAMINES

Substance	Found, wt. %		
	Hydroxyamine	H_2O	Total
Monoethanolamine (6)[a]	99.8 ± 0.1	0.1	99.9
Diethanolamine (4)	99.9 ± 0.1	.0	99.9
Triethanolamine[b] (4)	99.9 ± 0.1	.0	99.9
Diisopropanolamine (2)	100.1 ± 0.1	.7	100.8
Triisopropanolamine (2)	95.0 ± 0.4	.2	95.2
2-Amino-2-methyl-1-propanol[c] (4)	99.6 ± 0.2	.3	99.9
Hydroxyethyl ethylenediamine (2)	97.8 ± 0.3	.6	98.4
2-Amino-2-methyl-1,3-propanediol[c] (4)	99.5 ± 0.4	.0	99.5
2-Amino-2-ethyl-1,3-propanediol[c] (4)	89.9 ± 0.5	.4	90.3
2-Amino-1-butanol[c] (4)	96.5 ± 0.3	1.6	98.1
Tris-(hydroxymethyl)-aminomethane[c] (4)	99.2 ± 0.2	.0	99.2
Ethylphenylethanolamine (2)	96.7 ± 0.2	.4	97.1

[a] Figures in parentheses represent number of determinations. [b] Eastman Kodak Chemical. [c] Commercial Solvents Company, all others Carbide & Carbon chemicals.

The analytical method was developed through a study of the esterification of carefully purified

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(1) Presented in part before the Division of Analytical and Micro Chemistry at the Pittsburgh Meeting of the American Chemical Society, September 9, 1943.

(2) Smith and Bryant, THIS JOURNAL, **57**, 61 (1935).

(3) Christensen, Pennington and Dimick, *Ind. Eng. Chem. Anal. Ed.*, **13**, 821 (1941).

(4) Verley and Bölsing, *Ber.*, **34**, 3354 (1901).

(5) Bryant, Mitchell and Smith, THIS JOURNAL, **62**, 1 (1940).

(6) Obtained in cylinders from the Ohio Chemical Company, Cleveland, Ohio.

(7) Smith, Bryant and Mitchell, THIS JOURNAL, **61**, 2407 (1939).

(8) Where convenient the sample, containing up to 10 milliequivalents of hydroxyl, may be weighed directly into the 250-ml. volumetric flask. In this case 5 ml. of glacial acetic acid should be added to the cooled flask containing the sample before addition of the reagent.

mono- and diethanolamines, using various concentrations of boron trifluoride in acetic acid with ten milliequivalents of hydroxyl. Results obtained are shown in Table II.

TABLE II

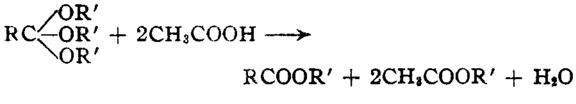
EFFECT OF CONCENTRATION OF BF_3 ON ESTERIFICATION OF ETHANOLAMINE

	% Reaction of —OH group		
	50 g. BF_3/l.	100 g. BF_3/l.	200 g./l.
Monoethanolamine	38	96	99.8
Diethanolamine	79	96	99.9

It is interesting to note that in the experiment using 50 g. of boron trifluoride per liter the reaction of diethanolamine was considerably greater than the monoethanolamine.

Interfering Substances.—The new hydroxyl procedure is unfavorably affected by aldehydes and ketones, acetals and ketals as indicated in an earlier publication.[5]

Orthoesters react quantitatively. The reaction apparently is general, probably following the equation



$$RC\begin{matrix}\diagup OR'\\ -OR'\\ \diagdown OR'\end{matrix} + 2CH_3COOH \longrightarrow RCOOR' + 2CH_3COOR' + H_2O$$

Five Eastman Kodak Co. orthoesters were mixed with the 100 g. of catalyst and heated for two hours at 60° and at 67°. Analytical results are summarized in Table III.

TABLE III

ANALYTICAL DATA ON ORTHOESTERS

Substance	Found, wt. %
Ethyl orthoformate	97.6 ± 0.4
Methyl orthoacetate	99.4 ± 0.3
Methyl orthopropionate	97.4 ± 0.0
Methyl ortho-*n*-butyrate	97.1 ± 0.0
Methyl ortho-*n*-valerate	92.2 ± 0.3

Summary

1. A specific quantitative method for the determination of hydroxyamines has been described. The method is based on quantitative esterification and subsequent titration of the water liberated with Karl Fischer reagent.

2. The method is applicable to the determination of hydroxyl in the presence of ammonia or amines.

3. Analytical results are reported for twelve amino alcohols.

4. The method is quantitative for samples containing a large excess of water.

5. Orthoesters react quantitatively with the acetic acid in the esterification reagent.

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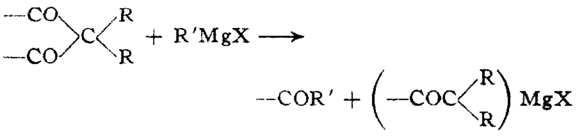
The Reaction between Cyclic β-Diketones and Grignard Reagents. II. 8,8-Dimethylperinaphthindandione-7,9[1]

BY T. A. GEISSMAN AND LESTER MORRIS

The reaction between cyclic β-diketones and Grignard reagents has been studied in a few cases only, and in none of these cases has the cleavage of the diketone been observed, normal addition of the reagent to the carbonyl groups having occurred.[2] This behavior is in marked contrast to that of many open-chain diketones, which are cleaved by the action of Grignard reagents according to the partial equation



$$\begin{matrix}—CO\diagdown\\ —CO\diagup\end{matrix}C\begin{matrix}\diagup R\\ \diagdown R\end{matrix} + R'MgX \longrightarrow —COR' + \left(—COC\begin{matrix}\diagup R\\ \diagdown R\end{matrix}\right)MgX$$

When the ketone represented by —COR′ is capable of further reaction with the reagent a tertiary alcohol is the final product.

In the present work the study has been extended to include a diketone in which the diketonic function is a part of a six-membered ring: 8,8-dimethylperinaphthindandione-7,9 (I). The reaction of this compound with phenylmagnesium bromide has been carried out under a variety of conditions and three products have been isolated and characterized. None of these is the expected cleavage product.

8,8-Dimethylperinaphthindandione-7,9 was prepared by the methylation (in two steps) of perinaphthindandione-7,9.[3] It has been described by Freund and Fleischer,[4] who prepared it by the condensation of naphthalene with dimethylmalonyl chloride under the influence of aluminum chloride, followed by manual separation of the crystals of the three possible isomers, all of which were produced. An unsuccessful attempt was made in the present work to prepare the monomethyl derivative by the condensation of ethyl propionate with methyl 1,8-naphthalate; although the expected product was formed the yield was very low.

By a suitable control of the experimental con-

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(1) Presented before the American Chemical Society, Fall Meeting, 1942, at Buffalo, N. Y.

(2) Geissman and Tulagin, THIS JOURNAL, **63**, 3352 (1941), and other references there cited.

(3) Errera, *Gazz. chim. ital.*, **41**, I, 190 (1911); *Chem. Centr.*, **82**, II. 1633 (1911).

(4) Freund and Fleischer, *Ann.*, **399**, 203 (1913).