

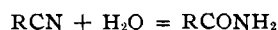
[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS &amp; COMPANY, INC.]

**Analytical Procedures Employing Karl Fischer Reagent. XIII. The Determination of Nitriles<sup>1</sup>**

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Nitriles usually are identified after acid or alkaline hydrolysis to the corresponding acid,<sup>2,3,4,5</sup> and in some cases alcoholysis<sup>6</sup> or reduction<sup>7,8</sup> has proved feasible. Direct identification has been based on the preparation of crystalline derivatives of the nitriles with mercaptoacetic acid<sup>9</sup> and phloroglucinol.<sup>10</sup> These methods were designed primarily for qualitative identification and consequently have not proved generally applicable to the quantitative estimation of nitriles.

In the present investigation a method has been developed which is based on quantitative hydrolysis of the nitrile to the corresponding amide



The nitrile is treated with an excess of water in the presence of boron trifluoride and acetic acid. After hydrolysis the unused water is titrated directly with Karl Fischer reagent. Net water between blank and sample is equivalent to the nitrile originally present.

The new method is generally suitable for the determination of normal alkyl cyanides. Quantitative results have been obtained on the normal lower aliphatic nitriles, nitriles of dibasic acids and several aromatic cyanides.

**Experimental**

**Reagents.**—The hydrolytic reagent is prepared by dissolving 300 g. of dry boron trifluoride gas and 6.5 ml. of water in 500 ml. of glacial acetic acid ( $\text{BF}_3 \cdot 2\text{CH}_3\text{CO}_2\text{H}$ ).<sup>11,12</sup> Karl Fischer reagent is prepared according to directions given in an earlier publication.<sup>13</sup>

**Analytical Procedure.**—The sample, containing up to 10 milliequivalents of nitrile, is weighed into a 250-ml. glass-stoppered volumetric flask. Twenty ml. of the hydrolysis reagent is added. The flask is tightly stoppered<sup>14</sup> and, together with duplicate blanks, placed in an oven or water-bath at  $80 \pm 2^\circ$  for two hours. At the end of this time the flasks are removed, allowed to cool spontaneously to room temperature, then placed in a container of finely chopped ice during the careful addition of 15 ml. of dry

pyridine.<sup>15</sup> The homogeneous solution is titrated directly with Karl Fischer reagent.

Since the nitrile group does not interfere, the sample can be titrated directly for free water. The net titer plus water originally present in the sample is a direct measure of the equivalents of cyanide.

**Analytical Results**

Several aliphatic and aromatic nitriles have been analyzed by this method. In general the precision and accuracy are within  $\pm 0.3\%$ . Experimental data are recorded in Table I. These chemicals were analyzed as received, without further purification. The number of representative nitriles for which a 100% balance is shown is considered sufficient for establishing the order of precision and accuracy. Those which totaled low were assumed to contain inert impurity.

TABLE I  
ANALYTICAL DATA FOR NITRILES

Nitrile		Found, wt. %		Total
		Nitrile	Water	
Acetonitrile	(10) <sup>a</sup>	97.6 $\pm$ 0.2	2.3	99.9
Propionitrile	(6)	98.7	.3	100.3
Cyanoacetamide	(2)	93.6	.4	94.4
<i>n</i> -Butyronitrile	(2)	99.0	.2	100.2
<i>n</i> -Valeronitrile	(2)	99.4	.0	99.8
Lauryl cyanide	(1)	97.7	.1	97.8
Adiponitrile <sup>b</sup>	(10)	99.8	.2	99.8
Sebaconitrile <sup>b</sup>	(4)	100.0	.4	100.0
Phenylacetoneitrile	(2)	99.6	.2	99.8
<i>m</i> -Toluonitrile	(2)	100.6	.2	100.7
<i>p</i> -Toluonitrile	(2)	100.8	.4	100.9
<i>p</i> -Chlorobenzonitrile	(2)	97.6	.3	97.7
$\beta$ -Naphthonitrile	(6)	96.5	.4	96.6

<sup>a</sup> Figures in parentheses represent number of individual determinations. <sup>b</sup> Du Pont; all others Eastman Kodak Co. chemicals used without further purification.

Other nitriles were found to give incomplete but fairly precise results. Although *m*- and *p*-toluonitrile and  $\beta$ -naphthonitrile reacted quantitatively, *o*-toluonitrile and  $\alpha$ -naphthonitrile gave values of  $89.5 \pm 0.5$  and  $80.9 \pm 0.2\%$ , respectively. Methyleneaminoacetoneitrile, presumably because of the inhibiting influence of the amino group, reacted only to the extent of  $80.9 \pm 0.2\%$  and cyanoacetoneitrile gave values of  $88.8 \pm 0.9\%$ . It is surprising that cyanoacetic acid<sup>16</sup> indicated only  $37.1 \pm 1.4\%$  reaction.

The new procedure was developed from a series of experiments with various acid and basic catalysts. Sulfuric acid was apparently satisfactory

(15) Pyridine is essential at this point. It combines with the boron fluoride thereby preventing esterification with the methanol during subsequent titration with the Karl Fischer reagent.

(16) Eastman Kodak Company practical.

(1) Presented in part before the Division of Analytical and Microchemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pennsylvania, September 9, 1943.

(2) Frankland and Kolbe, *Ann.*, **65**, 298 (1848).

(3) Angelescu, Vasiliu and Radvan, *Bull. sect. sci. acad. roumaine*, **22**, 220 (1939).

(4) Rovira and Palfray, *Compt. rend.*, **210**, 396 (1940).

(5) Rabinovitch and Winkler, *Can. J. Research*, **20B**, 221 (1942).

(6) Backunts and Otto, *Ber.*, **9**, 1590 (1876).

(7) Ladenberg, *ibid.*, **18**, 2596 (1885).

(8) Cutter and Tarras, *Ind. Eng. Chem., Anal. Ed.*, **13**, 830 (1941).

(9) Condo, Hinkel, Fassero and Shriner, *THIS JOURNAL*, **59**, 230 (1937).

(10) Howells and Little, *ibid.*, **54**, 2451 (1932).

(11) Meerwein, *Ber.*, **66B**, 411 (1933).

(12) Meerwein and Pannwitz, *J. prakt. Chem.*, [II] **141**, 123 (1934).

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

(14) Precision Scientific Co. #4799 spring clamps are convenient for this purpose.

but the precision was poor ( $\approx 5\%$ ). With high concentrations of boron fluoride in methanol variable dehydration occurred at elevated temperatures. Since alkalis react with the Karl Fischer reagent<sup>17</sup> only low concentrations could be tolerated which were insufficient for normal alkaline hydrolysis.

The effects of concentration of boron trifluoride in acetic acid, time and temperature on the hydrolysis of acetonitrile and adiponitrile are recorded in Table II.

TABLE II

Nitrile	Reagent, g. BF <sub>3</sub> /l.	Condition	% Reaction
Acetonitrile	100	1 hr., room temp.	3.5
	100	1 hr., 60°	9
	360	1 hr., 60	66
	360	2 hr., 60	91
	360	1 hr., 80	95
	360	2 hr., 80	100
Adiponitrile	360	1 hr., 60°	74
	360	2 hrs., 60	92
	360	1 hr., 80	97
	360	2 hrs., 80	100

**Interfering Substances.**—Materials which interfere with the Fischer hydroxyl procedure<sup>18</sup>

(17) Mitchell, Smith, Ashby and Bryant, *THIS JOURNAL*, **63**, 2927 (1941).

(18) Bryant, Mitchell and Smith, *ibid.*, **62**, 1 (1940).

also unfavorably affect the new nitrile technique. Alcoholic hydroxyl will esterify under these conditions, quantitatively eliminating an equivalent amount of water. Consequently, provided the hydroxyl content can be determined by an independent method,<sup>19</sup> suitable corrections to the nitrile value can be applied. Cyanohydrins hydrolyze readily. The normal hydroxyl esterification catalyst (100 g. BF<sub>3</sub>/l.)<sup>16</sup> was sufficient to hydrolyze acetaldehyde cyanohydrin to the extent of about 60%; the net increase in water after two hours at 65° was equivalent to about 40% of the hydroxyl. Under conditions of the general nitrile procedure, however, both reactions are quantitative giving a net water balance of zero.

Little interference is observed with amides. Formamide, acetamide and adipamide gave values of 0.0, 0.3 and 0.2% reaction, respectively.

The authors are grateful to Donald Milton Smith, under whose direction a portion of this work was carried out.

### Summary

1. A new method for the determination of nitriles based on hydrolysis in the presence of BF<sub>3</sub>·2CH<sub>3</sub>COOH, has been described.

2. Analytical results obtained on eighteen nitriles have been reported.

(19) The acetyl chloride method of Smith and Bryant, *ibid.*, **57**, 61 (1935), can be used in the absence of amino-nitrogen.

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## Dipole Moment and Structure of Organic Compounds. XVII.<sup>1</sup> The Electric Moments of $\alpha$ - and $\beta$ -Stilbene Dibromide and of *p*-Diacetylbenzene

BY A. WEISSBERGER

The electric moments of  $\alpha$ - and of  $\beta$ -stilbene dibromide which were communicated to and published by McCullough<sup>2</sup> have recently been referred to<sup>3</sup> with the apparent desire for publication of the results in detail.

The dipole moments of the compounds were determined in benzene by H. Müller ( $\alpha$ ) and R. Sängewald ( $\beta$ ), respectively. The electric moment of  $\alpha$ -stilbene dibromide is 0.4 to 0.9 *D*; that of  $\beta$ -stilbene dibromide is 2.8<sub>1</sub>*D*. Müller used methods for the determination of *d* and of  $\epsilon$  which he reported to permit the calculation of *P*<sub>2</sub> with the accuracy stated in the table, in spite of the low solubility of the  $\alpha$ -dibromide. Sängewald used the method described previously.<sup>4</sup> The materials were prepared according to Pfeiffer.<sup>5</sup> The  $\alpha$ -stilbene dibromide, recrystallized several times from dioxane, melted at 286°. The  $\beta$ -stilbene

dibromide, recrystallized repeatedly from hexane, melted at 110°.

The data of the measurements and calculations are given in the table. The symbols have the usual significance: *f*<sub>2</sub> = molecular percentage; *d* = density;  $\epsilon$  = dielectric constant; *n* = refractive index of the solutions; *P*<sub>2</sub> = total polarization, and *P*<sub>2</sub><sup>o</sup> = optical part of the total polarization of the solute.

It was shown earlier that the  $\beta$ -stilbene dichloride with the electric moment 2.7<sub>5</sub>*D*<sup>6</sup> is the *dl*-compound,<sup>7</sup> while the  $\alpha$ -stilbene dichloride with the electric moment 1.27<sup>8</sup> is the *meso*-compound.<sup>7</sup> By analogy with the dichlorides,  $\alpha$ -stilbene dibromide should be the *meso*-compound, while  $\beta$ -stilbene dibromide represents the *dl*-form. The difference in the moments of the dibromides is obviously similar in origin to the difference in the moments of the dichlorides.<sup>8</sup> It may be assumed that the greater volume of the

(1) XVI. G. C. Hampson and A. Weissberger, *THIS JOURNAL*, **58**, 2111 (1933).

(2) J. D. McCullough, *ibid.*, **62**, 480 (1940).

(3) D. Renlos, *Compt. rend.*, **216**, 774 (1943).

(4) A. Weissberger and R. Sängewald, *Physik. Z.*, **30**, 792 (1929).

(5) P. Pfeiffer, *Ber.*, **45**, 1810 (1912).

(6) A. Weissberger and R. Sängewald, *Z. physik. Chem.*, **B9**, 133 (1930).

(7) A. Weissberger and H. Bach, *Ber.*, **64**, 1095 (1931).

(8) A. Weissberger, *J. Org. Chem.*, **2**, 245 (1937).