but the precision was poor (±5%). With high concentrations of boron fluoride in methanol variable dehydration occurred at elevated temperatures. Since alkalies react with the Karl Fischer reagent[17] 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

FACTORS INFLUENCING THE HYDROLYSIS OF NITRILES

Nitrile	Reagent, g. BF_3/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[18] 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,[19] suitable corrections to the nitrile value can be applied. Cyanohydrins hydrolyze readily. The normal hydroxyl esterification catalyst (100 g. BF_3/l.)[16] 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 $BF_3 \cdot 2CH_3COOH$, has been described.

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

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

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

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

WILMINGTON, DELAWARE RECEIVED FEBRUARY 1, 1945

Dipole Moment and Structure of Organic Compounds. XVII.[1] The Electric Moments of α- and β-Stilbene Dibromide and of *p*-Diacetylbenzene

BY A. WEISSBERGER

The electric moments of α- and of β-stilbene dibromide which were communicated to and published by McCullough[2] have recently been referred to[3] with the apparent desire for publication of the results in detail.

The dipole moments of the compounds were determined in benzene by H. Müller (α) and R. Sängewald (β), respectively. The electric moment of α-stilbene dibromide is 0.4 to 0.9 *D;* that of β-stilbene dibromide is $2.8_1 D$. Müller used methods for the determination of d and of ϵ which he reported to permit the calculation of P_2 with the accuracy stated in the table, in spite of the low solubility of the α-dibromide. Sängewald used the method described previously.[4] The materials were prepared according to Pfeiffer.[5] The α-stilbene dibromide, recrystallized several times from dioxane, melted at 286°. The β-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_2 = molecular percentage; d = density; ϵ = dielectric constant; n = refractive index of the solutions; P_2 = total polarization, and P''_2 = optical part of the total polarization of the solute.

It was shown earlier that the β-stilbene dichloride with the electric moment $2.7_5 D$[6] is the *dl*-compound,[7] while the α-stilbene dichloride with the electric moment 1.2_7[6] is the *meso*-compound.[7] By analogy with the dichlorides, α-stilbene dibromide should be the *meso*-compound, while β-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.[8] It may be assumed that the greater volume of the

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[1] XVI. G. C. Hampson and A. Weissberger, THIS JOURNAL, **58**, 2011 (1936).

[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).

bromine atoms is responsible for the greater difference in the moments of the dibromides as compared with the dichlorides. The fact that the *dl*-stilbene dibromide has a moment higher than that to be expected for a random distribution about the ethane C–C link, again appears to be the result of London forces between the bromine atoms.[8,9]

The electric moment of *diacetyl* was calculated by Zahn[10] from the moments of the component groups. Assuming a random distribution around the C–C linkage (free rotation), the moment should be 3.2*D*. The same author found, experimentally, a moment which varies between 55° and 230° from 1.2_5 to 1.4_8D. These values and the temperature dependence itself indicate a considerable mutual interference of the two acetyl groups. With acetyl acetone, where a CH_2 group is inserted between the acetyl groups, complications arise from enolization.[10]

In *p*-diacetylbenzene the acetyl groups are separated by a benzene nucleus *p*-Diacetylbenzene was prepared according to the method of Berend and Herms.[11] It had a m. p. of 113–114°. The results of Sängewald's measurements and calculations are given in the table.

The electric moment of *p*-diacetylbenzene, 2.7_1D, is much closer to that calculated for diacetyl than the moment of diacetyl itself. However, it is still about 15% lower than the calculated value. According to Smyth,[12] resonance may give sufficient double bond character to the bond between the acetyl group and the ring to favor *cis-* and *trans*-forms. The observed moment would then depend upon the relative stability of the two forms.

Attempts by Sängewald to measure the moment of 4,4′-diacetyldiphenyl were frustrated by the low solubility of the compound.

TABLE I

MEASUREMENTS IN BENZENE

f_2, %	d_4^t	ε	n^2	$P_{1,2}$	$P''_{1,2}$
α-Stilbene dibromide, $t = 20.0 \pm 0.1°$					
0	0.878825	2.28400		26.6173	
0.00918	.878985	2.284325		26.6241	
.01578	.879105	2.284166		26.6254	
$dP_{1,2}/df_2 \sim 70$, $P_2 = 90 \pm 10$, P_2'' calcd. $= 76$, $\mu = 0.4 - 0.9D$					
β-Stilbene dibromide, $t = 25.0 \pm 0.1°$					
0	0.8735	2.272	2.2443	26.610	26.194
0.3004	.8782	2.311	2.2476	27.298	26.366
.4122	.8803	2.320	2.2482	27.463	26.409
.5331	.8828	2.340	2.2497	27.786	26.464
$dP_{1,2}/df_2 = 216$, $dP_{1,2}''/df_2 = 53.4$, $P_2 = 243$, $P_2'' = 79.6$, $\mu = 2.8_1D$					
Diacetylbenzene, $t = 25.0 \pm 0.1°$					
0	0.8731	2.282	2.2427	26.763	26.184
0.6294	.8757	2.339	2.2446	27.688	26.310
0.9624	.8771	2.383	2.2455	28.368	26.377
1.325	.8786	2.433	2.2473	29.126	26.460
$dP_{1,2}/df_2 = 172$, $dP_{1,2}''/df_2 = 20.8$, $P_2 = 199$, $P_2'' = 46.9$, $\mu = 2.7_1D$					

Summary

The electric moments of the stilbene dibromides and of *p*-diacetylbenzene are determined and discussed.

It is concluded from the moments of the stilbene dibromides that α-stilbene dibromide is the *meso*-compound and β-stilbene dibromide is the *dl*-compound.

ROCHESTER, N. Y. RECEIVED FEBRUARY 24, 1945

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(9) G. C. Hampson and A. Weissberger, THIS JOURNAL, **58**, 2111 (1936).

(10) C. T. Zahn, *Physik. Z.*, **34**, 570 (1933).

(11) W. Berend and P. Herms, *J. prakt. Chem.*, [2] **74**, 134 (1906).

(12) C. P. Smyth, private communication.

[CONTRIBUTION FROM SEROLOGICAL LABORATORY, UNIVERSITY HOSPITAL, UNIVERSITY OF MICHIGAN]

The Effect of Haptens on Serological Precipitates, with Experimental Data on Kahn Precipitates

BY J. DAVID NEWBURGH

Theoretical Considerations

Various methods have been suggested to describe the amount of antigen–antibody precipitate in terms of the amounts of antigen and antibody present. The method used here, *i. e.*, the use of the fundamental laws of equilibrium, has recently been advocated by Pauling and others.[1] For definiteness, we consider antigen molecules, A, which have two regions, each of which is capable of forming specific bonds with the antibody, B. The antibody is also considered bivalent. The combination of the antibody with one of these two groups of the antigen is taken to be independent of whether or not the other group is free or combined with an antibody molecule. H represents a monovalent hapten, *i. e.*, it has one group capable of being bonded to the antibody. The composition of the precipitate will be $(AB)_n$, *n* being a large number; its amount is represented by AB_{pp} and its solubility by *s*. The total amounts of antigen, antibody, and hapten will be indicated by A_t, B_t, and H_t, respectively. For convenience, several concentrations are abbreviated as follows:

$[A] = \alpha$ $[B] = \beta$ $[H] = \eta$
$[AB] = s$ $[A_2B] = a$ $[AB_2] = b$
$[BH] = h$ $[BH_2] = k$

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(1) L. Pauling, D. Pressman, D. H. Campbell and C. Ikeda, THIS JOURNAL, **64**, 3003 (1942); and Pauling, Campbell and Pressman, *Physiol Rev.*, **23**, **203** (1943).