The thermometer rose rapidly from 120° to 220°. No evidence of benzylethyl ether was found. The fraction from 220° to 280° was identified as diphenylmethane. No investigation was made for the oil which came over between 235° and 350° at 30 mm.

Chloromethylethyl Ether and Aluminum Chloride.—Fourteen grams of chloromethylethyl ether were placed in a flask fitted with a calcium chloride tube and treated with an excess (22 g.) of aluminum chloride in small amounts. A vigorous reaction set in, heat was evolved, and hydrochloric acid was given off rapidly. After standing overnight, all reaction seemed to have ceased. The flask contained a reddish brown syrup and some unchanged aluminum chloride. The whole was poured into ice water. A small amount of volatile oil came to the surface. The aqueous solution smelled strongly of formaldehyde. A portion was just neutralized with NaOH and filtered. A piece of filter paper, moistened with ammoniacal silver nitrate solution, was turned black when held over the warmed filtrate.

EAST LANSING, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE.]

THE MOLECULAR WEIGHT OF SOME ALCOHOLATES OF CHLORAL AND BUTYLCHLORAL IN BENZENE SOLUTION.

BY MARGUERITE WILLCOX AND ROGER F. BRUNEL.

Received September 16, 1916.

The partial dissociation of chloralethylalcoholate into its constituents when dissolved in organic solvents, first investigated by Beckman,[1] was more extensively examined by Willcox and Brunel in a recent article,[2] in connection with an investigation of the replacement of one alcohol by another in such alcoholates. It has now been found that other alcoholates of chloral and butylchloral are likewise, as would be expected, somewhat dissociated in solution.

An examination of Table II, p. 1827, in the above paper by the authors, and of the reactions on which it is based, make evident certain conclusions as to the relative tendency to dissociation which these alcoholates of various alcohols should exhibit. It is there concluded that as we pass downward in the table, in the list of alcohols there studied, the affinity of the alkyl groups for the hydroxyl becomes relatively greater than their affinity for the chloral and butylchloral radicals. The tendency of the alcohols to form alcoholates with the aldehydes, involving separation of the alkyl group from the hydroxyl, should, therefore, decrease in this order, so that the degree of dissociation of the alcoholates should increase as we pass downward in the list of alcohols it this table. The following experiments show

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[1] *Z. physik. Chem.*, **2**, 724 (1888).

[2] THIS JOURNAL, 38, 1821 (1916).

this to be the case, the alcoholates of primary alcohols being least highly, those of tertiary alcohols most highly dissociated, with those of secondary alcohols falling between them. The concentrations are not the same for all of them, but are sufficiently close to make the relationship clear.

The purest benzene obtainable was frozen out four times, dried with calcium chloride and phosphorus pentoxide, and distilled. B. p. 79.4. The value 4.9 was used for the constant. The concentrations are given in per cent. by weight.[1]

Solute.	Δ.	Per cent. conc.	Mol. wt.		Per cent. dissociation.
			Calc.	Found.	
Chloralethylalcoholate	0.543°	2.00	193	189	2.30
	1.276	4.77		197	Assocd.
Chloral-*l*-amylalcoholate	1.547	6.815	235	232	1.29
	1.539	6.812		232	1.29
Chloral methylpropylcarbinolate	1.440	6.21	235	225	4.00
Chloral-*t*-amylalcoholate	1.460	5.94	235	212	10.8
Butylchloralethylalcoholate	1.728	6.82	221	208	6.25
	2.945	12.38		235	Assocd.
Butylchloral-sec.butylalcoholate	1.087	4.41	250	208	20.2
	2.167	8.976		223	12.0
Butylchloral-*t*-amylalcoholate	2.715	6.29	264	198	33.3

If some of these more highly dissociated alcoholates underwent some dissociation in the equilibrium experiments of the earlier paper by the authors, above referred to, it would have to be taken into account in order to determine the true equilibrium between the molecular forms of the alcoholates. A little consideration will show that it could not affect the order in which the alcohols would fall in the series there studied, but would merely accentuate the differences in the end points which would be found if the dissociation were negligible in amount.

It cannot be stated with certainty whether or not such dissociation occurred. The concentration of the tertiary alcoholates fell, in the chloral series, as low as 2 g., that of butylchloral-*d*-sec.butylalcoholate in some cases as low as 9 g. per hundred cc. of solution. Expressed as per cent. by weight both of these values would be somewhat higher. These are concentrations at which the alcoholates concerned should be somewhat dissociated. But it must be kept in mind that there were always two such alcoholates present when equilibrium was reached giving a common dissociation product, and it is reasonable to assume that some suppression of the dissociation of each would occur. If we assume that we may apply the principle frequently employed in the case of electrolytic dissociation, according to which each substance dissociates as if it were present occupying

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[1] In the former paper the words under the curve, *loc. cit.*, p. 1835, "percentage concentration," should read "Grams solute per 100 g. solvent," that being the manner of designating the concentrations in all of the molecular weight determinations in that paper.

a part of the total volume of the solution corresponding to its own mol. fraction of the dissociating substance present; and if we keep in mind the fact that the total amount of dissociating substance in the solutions in the equilibrium experiments was always 30% or more, it appears improbable that any considerable degree of dissociation could have occurred there.

BRYN MAWR, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

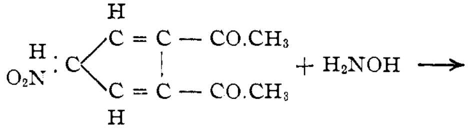
STUDIES IN THE CYCLOPENTADIENE SERIES. IV. THE FORMATION OF CYCLOPENTADIENODIHYDROPYRIDAZINES.

BY WILLIAM J. HALE.

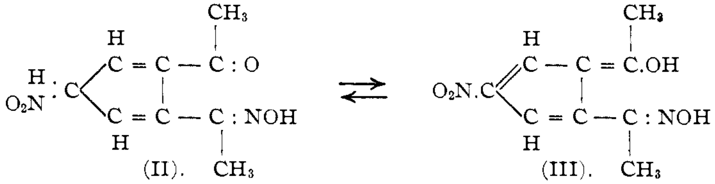
Received September 19, 1916.

In an earlier publication[1] upon 5-nitro-2,3-diacetylcyclopentadiene, attention was called to the fact that only one of the acetyl groups could be involved in the formation of oximes, anils or hydrazones. In a second publication[2] upon 5-nitro-2,3-dibenzoylcyclopentadiene the same general results were experienced. The possibility of steric hindrance interfering with the reaction of hydroxylamine or the hydrazines upon carbonyl groups attached to adjacent carbon atoms presented its usual doubtful significance; its elimination from consideration however followed immediately the study of these monohydrazones.

When, for example, one of the carbonyl groups of diacetylcyclopentadiene (I) enters into reaction there occurs a rearrangement of affinity; a rearrangement from that condition of equilibrium, where either one or the other of these carbonyl groups may exist transitorily in enolic form, to a condition stabilized with reference to one carbonyl group now involved with the basic nitrogen as oxime or hydrazone. The double linking thus established between the nitrogen and the carbon, with the consequent alternate double and single linkings around the ring, leads directly to the enolic form (III) of the second carbonyl group, a form naturally



(I).



(II). (III).

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[1] THIS JOURNAL, 34, 1583 (1912).

[2] *Ibid.*, 35, 70 (1913).