[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

Condensation between Formaldehyde and Monoketones. II

BY KONOMU MATSUMURA

In continuation of the study of the condensation between aminomonoketone and formaldehyde[1] the following additional instances are presented in this paper.

On the reaction with formaldehyde: (1) *p*-aminoacetophenone yields ω-hydroxymethyl-*p*-methylideneaminoacetophenone along with *p*-methylideneaminoacetophenone.

$$NH_2C_6H_4COCH_3 \longrightarrow CH_2{=}NC_6H_4COCH_2CH_2OH + CH_2{=}NC_6H_4COCH_3$$

(2) *p*-Dimethylaminodesoxybenzoins (α and β) give products which contain an hydroxymethyl group.

$$\underset{\beta}{(CH_3)_2NC_6H_4COCH_2C_6H_5} \longrightarrow (CH_3)_2NC_6H_4CO\underset{\displaystyle CH_2OH}{CH}C_6H_5$$

$$\underset{\alpha}{(CH_3)_2NC_6H_4CH_2COC_6H_5} \longrightarrow (CH_3)_2NC_6H_4\underset{\displaystyle CH_2OH}{CH}COC_6H_5$$

TABLE I

CONDENSATION PRODUCTS OF AMINOKETONES AND FORMALDEHYDE

Abbreviations: EtOH, alcohol; bz, benzene; chl, chloroform; S, soluble; i, insoluble

No.	Products	Yield, g.	Form	Solvent	M. p., °C.	Solubility
I	*p*-Methylideneamino-ω-hydroxymethyl-acetophenone	0.3	Colorless prisms	EtOH	218–219	S in bz and chl; i in ether and H_2O
II	*p*-Methylideneamino-ω-acetoxymethyl-acetophenone		Colorless needles	Ether	167	
III	*p*-Methylideneamino-acetophenone[a]	.2	Colorless needles	EtOH	192–193	S in bz, chl and H_2O; i in ether
IV	4-Dimethylamino-7-hydroxymethyldesoxybenzoin (α)	.7	Yellow needles	H_2O	110–111	S in organic solvents
V	4-Dimethylamino-7-benzoyloxymethyl-desoxybenzoin (α)		Yellow prisms	EtOH	135–136	
VI	4-Dimethylamino-7′-hydroxymethyldesoxybenzoin (β)	.9	Colorless needles	H_2O	132–133	S in organic solvents
VII	4-Dimethylamino-7′-benzoyloxymethyl-desoxybenzoin (β)[c]		Colorless prisms	EtOH	176–177	
VIII	ω-Methylene-bis-5-propionyl-8-hydroxy-quinoline	1.2	Colorless plates	NO_2-C_6H_5	166–267	S in chl
IX	Mono-oxime of VIII		Colorless plates	NO_2-C_6H_5	246–248 (dec.)	
X	Di-oxime of VIII		Colorless prisms	NO_2-C_6H_5	266–267 (dec.)	
XI	Hydrochloride of VIII		Orange needles	HCl (10%)	Liberates HCl at 150–160°. Hydrolyzes in H_2O	

No.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
I	$C_{10}H_{11}O_2N$	67.80	68.03	6.21	6.22	7.91	7.74
II	$C_{12}H_{13}O_3N$	65.75	65.59	5.94	6.36		
III	C_9H_9ON	73.47	73.48	6.12	6.13	9.52	9.36
IV	$C_{17}H_{19}O_2N$	75.84	75.95	7.06	7.21	5.20	5.40
V	$C_{24}H_{23}O_3N$	77.21	77.47	6.17	6.40	3.75	3.91
VI	$C_{17}H_{19}O_2N$[b]	75.84	77.02	7.06	7.25	5.20	5.17
VII	$C_{24}H_{23}O_3N$	77.21	77.61	6.17	6.44	3.75	3.87
VIII	$C_{25}H_{22}O_4N_2$	72.46	72.69	5.31	5.49	6.76	6.83
IX	$C_{25}H_{23}O_4N_3$					9.79	10.12
X	$C_{25}H_{24}O_4N_4$	67.57	67.76	5.40	5.62	12.61	12.68

No.	Formula		Calcd.	Found		Calcd.	Found
XI	$C_{25}H_{22}O_4N_2{\cdot}1.5HCl{\cdot}5H_2O$	H_2O	16.11	16.99	HCl	9.79	9.76

[a] Was obtained on concentrating the alcoholic filtrate of I. [b] The discrepancy of carbon contents may perhaps be due to impurity which could not be eliminated by repeated recrystallizations. [c] On refluxing this compound with alcoholic potash for two hours, the product gives light yellow prismatic needles from nitrobenzene, m. p. 252°. Its red solution in concd. sulfuric acid develops violet color on dilution with water. (*Anal.* C, 81.12, 80.86; H, 7.31, 7.22; N, 5.94, 5.89.) When similarly treated, VI afforded the same product.

(1) Matsumura, THIS JOURNAL, 53, 1490 (1931).

(3) 5-Propionyl-8-hydroxyquinoline gives ω-methylene-bis-5-propionyl-8-hydroxyquinoline.

$$(C_9H_6NO)COCH_2CH_3 \longrightarrow \begin{array}{l}(C_9H_6NO)COCHCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\; CH_2 \\ \qquad\qquad\quad | \\ (C_9H_6NO)COCHCH_3\end{array}$$

Experimental

A solution of aminomonoketone (1 g.) in formalin (40% 6–10 cc.) was refluxed on a water-bath for two to three hours, excess formaldehyde removed by evaporation as far as possible and water added. The resulting sirupy mass became solid on standing.

In the case of *p*-dimethylaminodesoxybenzoins, pyridine (10 cc.) was added as a solvent in the reaction.

In conclusion, the author desires to thank Professor Hata for the interest in this work and Professor Goto for the suggestion at which this work was done.

Summary

1. Condensation of 5-propionyl-8-hydroxyquinoline with formaldehyde gives ω-methylene-bis-5-propionyl-8-hydroxyquinoline.

2. Condensation of formaldehyde either with *p*-aminoacetophenone or with *p*-dimethylamino-desoxybenzoins (α and β) gives the compounds which have an hydroxymethyl group.

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The Dyeing of Cotton: Particle Size and Substantivity. I

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Introduction

Recent studies[1–5] of the dyeing of cotton with direct or substantive dyes emphasize the relation between the degree of dispersion of the dye and its characteristic dyeing properties. The particle size of dyes has been frequently calculated from the rate of diffusion by the Einstein[6] equation

$$D = RT/N \times 1/6\pi\eta r \qquad (1)$$

The correct estimation of the degree of dispersion of substantive dyes by this equation is possible only by careful consideration of the factors arising in the diffusion of colloidal electrolytes. Williams and Cady[7] recently surveyed the literature on diffusion measurements and their application to the estimation of particle size. Doubt as to the exact shape of the colloidal masses raises question as to the absolute accuracy of equation (1) in estimating the size of dye particles. Herzog, Illig and Kudar[8] showed that the error caused by assuming the particles to be spheres is relatively small except in cases involving extreme elongation. Hartley and Robinson[9] proved theoretically that diffusion constants of electrolyte free dyes of the type NaR are no criterion of their particle size. This fact has been used as a basis of criticism by Robinson[10] and by Neale[11] of previous work on the degree of dispersion of dyes. However, Hartley and Robinson[9] state that a relatively accurate estimate of the particle size is possible in the presence of large concentrations of inorganic electrolytes containing a common ion. Two methods are generally used for determining diffusion constants of dyes: (1) diffusion into gelatin, and (2) free diffusion into water. The methods are not applicable at the elevated temperatures used in dyeing processes. The known marked difference in the dyeing properties of substantive dyes at varying temperatures makes a study of particle size variation with temperature a matter of extreme importance. The diffusion method of Northrop and Anson,[12] used by McBain and others,[13] depends on the rate of diffusion through a porous diaphragm after a uniform concentration gradient is estab-

(1) Kurt and Brass, *Kolloid-Beihefte*, **37**, 56 (1932).
(2) Lenher and Smith, *Ind. Eng. Chem.*, **27**, 20 (1935).
(3) Schäffer, *Z. angew. Chem.*, **46**, 618 (1933).
(4) Schramek and Götte, *Kolloid-Beihefte*, **34**, 318 (1932).
(5) Rose, *Am. Dyestuff Reptr.*, **21**, 52 (1932).
(6) Einstein, *Ann. Physik*, **17**, 549 (1905).
(7) Williams and Cady, *Chem. Rev.*, **14**, 171 (1934).
(8) Herzog, Illig and Kudar, *Z. physik. Chem.*, **167A**, 329 (1934).
(9) Hartley and Robinson, *Proc. Roy. Soc.* (London), **A134**, 20 (1931).
(10) Robinson, *J. Soc. Dyers Colourists*, **50**, 171 (1934).
(11) Neale, *Am. Dyestuff Reptr.*, **22**, 237 (1933).
(12) Northrop and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).
(13) McBain and Liu, THIS JOURNAL, **53**, 59 (1931); McBain and Dawson, *ibid.*, **56**, 52 (1934).