TABLE I

RESULTS OBTAINED ON COUPLING DIAZOTIZED AMINES WITH VARIOUS COMPOUNDS

Component A	Component B	Product	M. p. °C.	B. p. °C.	Yield %
Aniline	Benzene	Biphenyl	70.5	.....	22
Aniline	Thiophene	Phenylthiophene	42–43	.....	11
Aniline	Cyanobenzene	*p*-Cyanobiphenyl	88	.....	10
Aniline	Bromobenzene	*o*- and *p*-Bromobiphenyl	.....	.....	..
Aniline	Methyl benzoate	Methyl *p*-phenyl-benzoate	116.5	.....	..
Aniline	Nitrobenzene	*p*-Nitrobiphenyl	113	.....	..
Aniline	Pyridine	Phenylpyridine	54–55	.....	..
p-Bromo-aniline	Benzene	*p*-Bromobiphenyl	91.2	.....	40–46
p-Bromo-aniline	Thiophene	**p*-Bromophenyl-thiophene	100	.....	20
m-Bromo-aniline	Benzene	**m*-Bromobiphenyl	.....	299–301	28
p-Chloro-aniline	Benzene	*p*-Chlorobiphenyl	77.7	.....	41
p-Chloro-aniline	Thiophene	**p*-Chlorophenyl-thiophene	83	.....	24
m-Chloro-aniline	Benzene	**m*-Chlorobiphenyl	.....	284–285	27
p-Nitro-aniline	Benzene	*p*-Nitrobiphenyl	114	.....	30
p-Nitro-aniline	Thiophene	**p*-Nitrophenyl-thiophene	137–138	.....	23
m-Nitro-aniline	Benzene	*m*-Nitrobiphenyl	61	.....	18
o-Nitro-aniline	Benzene	*o*-Nitrobiphenyl	36.7	.....	..
p-Cyano-aniline	Benzene	*p*-Cyanobiphenyl	88	.....	15
m-Cyano-aniline	Benzene	**m*-Cyanobiphenyl	49	.....	19
m-Cyano-aniline	Thiophene	**m*-Cyanophenyl-thiophene	53–54	.....	15
p-Aminobiphenyl	Benzene	*p*-Diphenylbenzene	209–210	.....	..
Ethyl-*p*-amino benzoate	Benzene	*p*-Phenyl-ethyl benzoate	50	.....	12

Compounds marked with an asterisk are those prepared for the first time.

Summary

When diazonium salts in aqueous solution are neutralized, a slight excess of the alkali activates the diazo hydroxides in such a manner that now they can couple with aromatic hydrocarbons and various derivatives therefrom. A large number of unsymmetrical biaryls have thus been prepared, many for the first time. The yields vary with the individual components that partake in the coupling process.

ANN ARBOR, MICHIGAN

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THE HYDROLYSIS OF AURAMINE

BY WALTER C. HOLMES[1] AND J. FERRIS DARLING[2]

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Under favorable conditions auramine is readily hydrolyzed in aqueous solution, with the formation of tetramethyl-*p*-diamino-benzophenone (Michler's ketone) and ammonium chloride. The factors which influence the hydrolysis are of obvious practical interest to those concerned in the manufacture or application of the dye.

The volumetric method for the estimation of the dye by means of titration with a standard solution of indigotin, in the manner proposed by

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[1] Associate Chemist, Color Laboratory, Bureau of Chemistry.

[2] E. I. du Pont de Nemours and Company.

one of the authors,[3] proved admirably adapted for the quantitative investigation of the reaction.

Influence of Temperature

The influence of temperature upon the hydrolysis of the dye in neutral solution was investigated with two samples of auramine, of which the first (1) was a relatively pure product obtained by the recrystallization of Du Pont auramine from aqueous solution and the second (2) a sample of auramine O (Berlin) containing about 40% of dye standardized with salt and Glauber's salt. Several different solutions of indigotin were used in the titrations. In all tests 0.5 g. of dye was employed in a solution volume of 250 cc. of distilled water. At the conclusion of the reaction period all solutions were cooled rapidly to room temperature and titrated immediately.

The results obtained are recorded in Table I.

TABLE I

INFLUENCE OF TEMPERATURE UPON THE HYDROLYSIS IN NEUTRAL SOLUTIONS

Sample	Temp. °C.	Time Hrs.	Original titration value Cc. of indigotin	Final titration value Cc. of indigotin	Velocity constant K	Half conversion period Hrs.
1	30	48	45.0	43.4	0.00075	920
1	40	6	36.9	36.4	.0023	309
1	45	4.5	44.1	43.1	.0051	135
1	50	2.67	36.9	36.0	.0092	75
1	60	2.5	36.9	34.8	.0234	29.6
2	60	3.0	27.5	25.6	.0215	32.2
2	60	3.0	27.5	25.4	.0250	27.7
2	60	3.0	27.5	25.5	.0226	30.7
				Av.	.0231	
2	70	2.0	27.5	24.6	.0557	12.4
2	70	2.0	27.5	24.7	.0554	12.6
2	70	2.0	27.5	24.6	.0557	12.4
				Av.	.0556	
1	80	1.0	38.45	33.9	.126	5.50
2	90	1.0	27.5	21.2	.260	2.66
2	90	1.0	27.5	20.8	.279	2.48
2	90	1.0	27.5	20.7	.284	2.44
				Av.	.274	
1	100	0.5	38.45	29.2	.550	1.26
1	100	6.5	36.9	00.8	.589	1.17
2	100	1.0	27.5	15.3	.586	1.18
2	100	1.0	27.5	15.5	.573	1.21
2	100	1.0	27.5	15.5	.573	1.21
2	100	1.0	27.5	15.7	.561	1.23
				Av.	.572	

The velocity constant (K) is calculated from the formula for a unimolecular reaction.

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[3] Holmes, *Color Trade J.*, **13**, 45 (1923).

$$\frac{dx}{dT} = K\,(a - x) \qquad (1)$$

in which K is the velocity constant at any given temperature, T the time in hours, a the initial concentration of dye and $a-x$ the final concentration of dye after time T. On integration this gives

$$K = \frac{1}{T} \log \left(\frac{a}{a-x}\right) \times 2.3026 \qquad (2)$$

In the calculation the ratio of the original and final titration values of the solutions is employed in place of that of the initial and final concentrations.

The figures recorded in the final column are for the time necessary to reduce the concentration of dye to one-half its initial value.

$$t = \frac{0.69314}{K} \text{ if } x = \frac{a}{2} \qquad (3)$$

The van't Hoff equation

$$\frac{d\,ln\,\frac{K}{K^1}}{dT} = \frac{U}{RT^2} \qquad (4)$$

(where K and K^1 are the opposing reaction velocities of the system in equilibrium) cannot be applied directly in the present case because we are measuring $K - K^1$, and since the reaction goes practically to completion K^1 may be neglected in comparison with K.

According to Nernst,[4] Equation 4 can be expressed in two general forms

$$\frac{d\,ln\,K}{dT} = \frac{C}{T^2} + B \qquad (5)$$

$$\frac{d\,ln\,K^1}{dT} = \frac{C^1}{T^2} + B \qquad (6)$$

where C and C^1 are constants and B is an arbitrary temperature function which may often be zero. Assuming that $B = 0$ and integrating (5), we have

$$\frac{ln\,K}{dT} = -\frac{C}{T} + A \qquad (7)$$

where C and A are constants, and finally

$$ln\,\frac{K_2}{K_1} \times \frac{T_1\,T_2}{T_2 - T_1} = C \qquad (8)$$

where K_1 and K_2 are reaction velocities at temperatures T_1 and T_2, respectively.

Values for C between 50° and 100°, as calculated from the average values obtained for K, are recorded in Table II.

Table II

Reaction Velocity-Temperature Constant

T	60	70	80	90	100	
T_2	50	60	70	80	90	
C	4302	4356	4299	4322	4328	Av., 4312

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[4] Nernst, "Theoretical Chemistry," MacMillan Co., 5th English ed., **1923,** pp. 771–772.

It is not apparent that the rate of hydrolysis was influenced in a measurable degree by the relative purity of the dye samples employed.

It appears probable that the adsorption of small quantities of dye by the containing vessels may have exerted a measurable effect on the apparent hydrolysis of the dye at moderate temperatures, and that the actual velocity of the reaction at temperatures below 60°, accordingly, may be somewhat lower than is indicated by the recorded data.

Influence of Acidity

The influence of acidity on the rate of hydrolysis is shown by the data in Table III. All tests were carried out at 100°, with Dye Sample 2. All titrations were made with a standard solution of indigotin, of which 27.5 cc. was equivalent to 0.5 g. of the auramine. The P_H values recorded apply to the solvents at room temperature but afford an approximate index of the hydrogen-ion concentrations of the various reacting solutions.

TABLE III

INFLUENCE OF ACIDITY ON THE HYDROLYSIS OF AURAMINE

Acidity	Approx. P_H	Time Hrs.	Final titration value Cc. indigotin	Velocity constant K	Half conversion period Hrs.
Neutral solution	7.0	1.0	15.3	0.586	1.18
	7.0	1.0	15.5	.573	1.21
	7.0	1.0	15.5	.573	1.21
	7.0	1.0	15.7	.561	1.23
0.29 g. of acetic acid	3.5	1.00	14.5	.640	1.08
	3.5	1.00	14.5	.640	1.08
	3.5	1.00	14.7	.626	1.11
0.009 g. of hydrochloric acid	3.0	1.00	13.5	.711	0.975
	3.0	1.00	13.6	.704	.985
	3.0	1.00	13.4	.719	.964
3.0 g. of acetic acid	2.9	1.0	11.0	.915	.757
	2.9	1.0	11.5	.872	.795
	2.9	1.0	11.4	.881	.787
0.07 g. of hydrochloric acid	2.2	0.167	16.0	3.25	.213
	2.2	.25	12.5	3.15	.220
	2.2	.25	12.7	3.09	.224
0.176 g. of hydrochloric acid	1.8	.083	8.5	14.09	.049
	1.8	.133	5.0	12.79	.054
	1.8	.083	9.0	14.56	.048
	1.8	.133	4.4	13.74	.050

The velocity of hydrolysis increases with the acidity and is clearly dependent primarily on the hydrogen-ion concentration of the solution. It is evident, moreover, that the catalytic activity of the hydrogen ions is stimulated by the presence of other ions. In these respects the hydrolysis of the dye resembles the inversion of cane sugar and the saponification of esters.

The dependence of the rate of hydrolysis of the dye upon the temperature and *P*H value of the solution is illustrated in Fig. 1.

Evaluation of the Dye by Hydrolysis

A reliable and relatively convenient volumetric method, which is of particular utility in the determination of auramine (or Auramine G) in admixture with other basic dyes, may be based upon its hydrolysis.

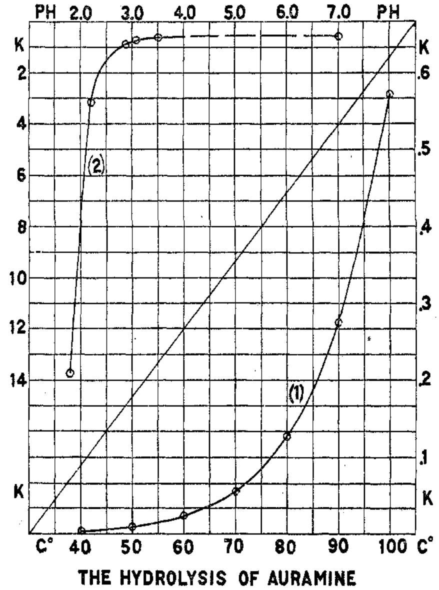

Fig. 1.—1 = Variation of K in neutral solution with change in temperature. 2 = Variation in K at 100° with change in *P*H.

When the dye is boiled with dil. hydrochloric acid, the hydrolysis proceeds nearly to completion in a brief period of time. (It does not appear possible to obtain complete hydrolysis in acid or neutral solution.) When the solution is made decidedly alkaline, the small quantity of residual dye is precipitated as the dye base. Upon further boiling, the ammonia derived from the hydrolysis of the dye (as ammonium chloride) passes over in the distillate and may be collected and measured in the usual manner. At the same time the dye base is hydrolyzed, with the formation of Michler's ketone and ammonia. As a final precaution it is advisable to wash down the sides of the distilling flask with alcohol and continue the distillation for a short time to preclude the possibility that very small quantities of dye base might otherwise escape hydrolysis.

Hydrolysis of Auramine G

With a sample of Auramine G (Geigy), values of 0.512, 0.512 and 0.509 were obtained for *K* in neutral solution at 100°. Under the same conditions values of 0.506, 0.504 and 0.500 were obtained with a Badische sample of the same dye. It is evident that Auramine G (Color Index No. 656) is appreciably more stable than auramine.

The authors wish to thank the Geigy Company, Inc., and Kuttroff, Pickhardt and Company, Inc., for their kindness in supplying samples of Auramine G.

Summary

(1) Data defining the dependence of the rate of hydrolysis of auramine in aqueous solution upon temperature and acidity have been recorded.

(2) A volumetric method which is of particular value in determining the quantity of auramines present in dye mixtures may be based upon their hydrolysis.

(3) Auramine G is appreciably more resistant to hydrolysis than is auramine.

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NEW BOOKS

Felix Cornu. (A memorial volume consisting of a biography, letters of appreciation, etc., from various chemists and geologists of Germany and Austria.) Theodor Steinkopff, Dresden and Leipzig, 1923. 148 pp. Illustrated. 23 × 16 cm. Price, unbound, 4 shillings.

Felix Cornu published about 57 papers on minerals, mineral chemistry, colloids, geology and geochemistry previous to his untimely death in 1909 at the age of 27. His contemporaries considered him a genial, brilliant, many-sided investigator. His energy for study developed early and burned like a meteor, ending abruptly. A brief biographical sketch by Becke appeared in *Min. pet. Mitt.*, **1909,** V Heft. These letters and the charming biography by his mother give more of personal interest and throw light on the influences of environment and heredity that affected Cornu. Felix was the son of a professor in the University of Prague. His uncle of the same name was a chemist and President of the *Société Vaudoise des Sciences Naturelles*, also a linguist and traveler, having twice visited the Cornu relatives in America. Cornu's death was a tragedy because much further was expected of him. His best known work is probably that on colloidal minerals and the colloidal matter in soils.

ROGER C. WELLS

Organic Chemistry for Advanced Students. By JULIUS B. COHEN, Ph.D., Professor of Organic Chemistry in the University of Leeds. Fourth edition. Longmans, Green and Company, New York; Edward Arnold and Company, London, 1923. Part I. Reactions. viii + 423 pp. 6 figs. Part II. Structure. vii + 461 pp. 68 figs. Part III. Synthesis. vii + 412 pp. 22.5 × 14 cm. Price, each part, $6.00.

The author has taken advantage of the new edition to incorporate a considerable amount of material which has appeared or become important since the text was revised for the second edition. Among the new subjects which are regarded as sufficiently important for special mention in the preface are the theories of Lewis and Langmuir and Sir J. J. Thomson on the structure of the atom, and their application to organic reactions; the work of Devine, Haworth and Hudson on the constitution of the carbohydrates; the developments of Baeyer's strain theory by Thorpe and Ingold; the photochemical studies of Baly and Heilbron; the bio-