It is probable that the rate-determining step in the general acid and basic catalysis of Brönsted is a transfer of hydrogen ion from acid catalyst to substrate similar to the transfer of methyl in the alkylation reaction.

These results are in agreement with the theory of simultaneous addition and dissociation in substitution reactions.
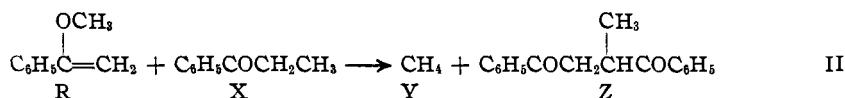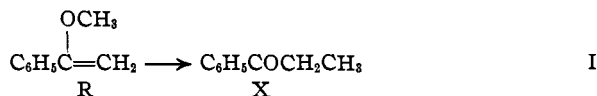
NEW YORK CITY

The Kinetics of the Rearrangement of α-Methoxystyrene[1]

BY F. H. MACDOUGALL, WALTER M. LAUER AND MARVIN A. SPIELMAN[2]

Claisen[3] has shown that α-methoxystyrene undergoes on heating a molecular rearrangement with the formation of propiophenone. A recent investigation[4] of the process has revealed an unusual type of side reaction. The unchanged starting material (R) reacts with the rearrangement product (X); a molecule of methane (Y) is eliminated and 1,2-dibenzoyl-propane (Z) results.

$$\overset{\overset{\textstyle OCH_3}{\textstyle |}}{C_6H_5C}=CH_2 \longrightarrow C_6H_5COCH_2CH_3 \qquad\qquad I$$
$$\quad\ \ R \qquad\qquad\qquad X$$

$$\overset{\overset{\textstyle OCH_3}{\textstyle |}}{C_6H_5C}=CH_2 + C_6H_5COCH_2CH_3 \longrightarrow CH_4 + C_6H_5COCH_2\overset{\overset{\textstyle CH_3}{\textstyle |}}{CH}COC_6H_5 \qquad II$$
$$\ \ R \qquad\qquad X \qquad\qquad\quad Y \qquad\qquad Z$$

In connection with a study of the mechanism of this type of molecular rearrangement, it became desirable to know the order of the reaction and to gain as much information as possible about the unique condensation reaction (II). While the mixture of compounds resulting from reactions I and II does not lend itself to highly precise methods of analysis, nevertheless a technique was developed whereby its composition could be determined with a fair degree of accuracy.

Experimental Methods

The thermostat was an upright Pyrex tube, 16×40 cm. rounded at the lower end and closed at the top with an asbestos cover. The lower two-thirds was wrapped with an asbestos jacket. Within was suspended a cylindrical aluminum block, 4.5×9 cm., in which were drilled five holes. An 8 mm. hole through the center bore a glass supporting rod and symmetrically disposed about it were four cylindrical holes. The diameter

(1) This paper is a portion of the thesis presented by Marvin A. Spielman to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Dupont Research Fellow in Chemistry, 1932–1933.

(3) Claisen, *Ber.*, **29**, 2931 (1896); Claisen and Haase, *ibid.*, **33**, 3778 (1900).

(4) Lauer and Spielman, THIS JOURNAL, **55**, in press (1933).

of these was 10 mm. except near the bottom where the bore was smaller.   Three of these holes held the sample tubes; the fourth hole held a thermometer.   A constant temperature was maintained by boiling about 50 cc. of an appropriate liquid at such a rate that the vapor condensed well above the aluminum block at a marked position above the insulating jacket.   The following liquids were used: diphenyl ether, b. p. 260.0 ± 0.3°; isosafral, b. p. 249.5 ± 0.4°; quinoline, b. p. 235.6 ± 0.5°; and methyl salicylate, b. p. 222.8 ± 0.6°.   Temperature measurements were made with Anschütz standard thermometers which were checked against instruments having Bureau of Standards calibrations.

Samples (about 0.8 g.) of freshly distilled, analytically pure α-methoxystyrene were weighed out into 8-cm. lengths of 8-mm. glass tubing sealed at one end.   These were filled with nitrogen, loosely stoppered and drawn out to 8-cm. capillaries which were sealed after room temperature was reached.   The liquid occupied about 80% of the volume of the reaction vessels.   Calculation shows that, even at the highest temperature employed less than one per cent. of the material is in the gas phase.   The tip was formed into a hook through which a light wire was passed to facilitate handling.   After they were removed from the thermostat, they were cooled and unsealed in a closed system connected to a gas buret.   Heating with a boiling water-bath served to expel the dissolved methane.   After cooling to room temperature, the volume of gas was determined over mercury.   The heating with the water-bath and the subsequent cooling were repeated until constant values were obtained for the volume of gas.

The residual liquid was then removed and analyzed for the methoxyl group by the Zeisel method, using the elegant volumetric modification of the method described by Viebock and Schwappach.[5]   In these determinations, check analyses were made and only those were used which agreed to within 0.2% OCH_3.   The percentages of α-methoxystyrene so obtained are probably correct to within one per cent.   In the measurement of the methane, gas buret readings could be duplicated to 0.01 cc. after heating and cooling, but the total volume of methane was in general small and there was always the danger that some of the methane might have been retained in the organic liquid.

We see from reaction equations I and II that, so long as all the methane formed remains in the liquid, there is no change in the total number of molecules.   The composition of the reaction mixture is expressed in mole fractions assuming all the methane to be dissolved.   Since in general the amount of methane formed is small, this procedure is sufficiently accurate.

Since some time is required to heat the reacting substance to the temperature selected for the experiment, a time correction is necessary.   This was determined graphically by plotting values of $1/R$ against the time and extrapolating back to a value of R equal to 1.   The time correction was found to be three minutes.   Accordingly all time values have been diminished by this amount.

For fuller details about experimental methods, the paper by Lauer and Spielman[4] may be consulted.

Kinetic Equations.—Let R, X and Y be the mole fractions of α-methoxystyrene, propiophenone and methane, respectively, in the reaction mixture at any time t.   We shall show that reactions I and II are of the second order.   On this basis, we have the following set of equations:

$$dR/dt = -k_1R^2 - k_2RX \qquad (1) \qquad dY/dt = k_2RX \qquad (3)$$
$$dX/dt = k_1R^2 - k_2RX \qquad (2) \qquad 1 = R + X + 2Y \qquad (4)$$

Of the equations (1), (2) and (3), only two are independent, because of the

(5) Viebock and Schwappach, *Ber.,* **63,** 2818 (1930).

relation expressed in equation (4). It will be convenient to make the substitutions

$$u = k_1 t \qquad (5) \qquad c = k_2/k_1 \qquad (6)$$

Equations (1), (2) and (3) become

$$dR/du = -R^2 - cRX \qquad (7) \qquad dY/du = cRX \qquad (9)$$
$$dX/du = R^2 - cRX \qquad (8)$$

R, X and Y are functions of u (or t) but cannot be expressed in terms of any simple function of u containing a finite number of terms. They can, however, be represented by infinite power series. The coefficients of the powers of u in the various series can be found by assuming an expansion $R = a_0 + a_1 u + a_2 u^2 \ldots$ and $X = b_0 + b_1 u + b_2 u^2 \ldots$ Substitution of these expressions in (7) and (8) leads to a knowledge of the coefficients. A less tedious method employs Maclaurin's theorem. If we denote the value of a function for $u = 0$ by the subscript zero, we have

$$R = R_0 + u(dR/du)_0 + u^2/2! \, (d^2R/du^2)_0 + u^3/3! \, (d^3R/du^3)_0 + \ldots \qquad (10)$$
$$X = X_0 + u(dX/du)_0 + u^2/2! \, (d^2X/du)_0 + u^3/3! \, (d^3X/du^3)_0 + \ldots \qquad (11)$$

Restricting ourselves to the case in which we start our reaction with pure α-methoxystyrene, we readily obtain from (4) and by repeated differentiation of (7) and (8) the results

$R_0 = 1$; $(dR/du)_0 = -1$; $(d^2R/du^2)_0 = 2 - c$; $(d^3R/du^3)_0 = -6 + 6c + c^2$;
$(d^4R/du^4)_0 = 24 - 36c - 4c^2 - c^3$; $(d^5R/du^5)_0 = -120 + 240c - 6c^2 - 4c^3 + c^4$;
$X_0 = 0$; $(dX/du)_0 = 1$; $(d^2X/du^2)_0 = -2 - c$; $(d^3X/du^3)_0 = 6 + 2c + c^2$
$\qquad (d^4X/du^4)_0 = -24 - c^3$; $(d^5X/du^5)_0 = 120 - 48c - 26c^2 - 8c^3 + c^4$

Similar procedures enable us to express in a power series in u any function of R or X, $e.\ g.$, $1/R$ and $1/(R+Y)$. We thus obtain the expansions

$$1/R = 1 + u + \frac{c}{2} u^2 - \frac{c^2}{6} u^3 + \frac{2c^2 + c^3}{24} u^4 - \frac{4c^2 + 6c^3 + c^4}{120} u^5 + \ldots \qquad (12)$$

$$1/(R + Y) = 1 + u - \frac{c}{3} u^3 + \frac{2c + 2c^2}{24} u^4 \ldots \qquad (13)$$

$$R = 1 - u + \frac{2 - c}{2} u^2 - \frac{6 - 6c - c^2}{6} u^3 + \frac{24 - 36c - 4c^2 - c^3}{24} u^4 + \ldots \qquad (14)$$

$$X = u - \frac{2 + c}{2} u^2 + \frac{6 + 2c + c^2}{6} u^3 - \frac{24 + c^3}{24} u^4 \ldots \qquad (15)$$

$$Y = \frac{c}{2} u^2 - \frac{4c + c^2}{6} u^3 + \frac{18c + 2c^2 + c^3}{24} u^4 \ldots \qquad (15a)$$

It will be shown that the value of $c = k_2/k_1$ is about 1/8. If we plot $1/R$ and $1/(R+Y)$ against u (or t), we shall obtain in the first place a curve which approximates to a straight line for small values of u but curves upward for larger values of u. In the second place (for the $1/(R+Y)$ curve), the curve will be more nearly straight over a greater range of u but should be slightly concave to the u axis. In Fig. 1 are plotted values of $1/R$ and $1/(R+Y)$ against t for the reaction at 260°. It will be seen that the curves for $1/R$ and $1/(R+Y)$ exhibit the predicted behavior. Figure 2 gives a graphic picture of the rate of formation of methane.

Equations (14) and (15) represent the values of R and of X, respectively, only for values of u less than unity. In all our experiments, the study of the reaction was extended to times for which u was greater than 2. These equations therefore can be applied only in the earlier stages of the reaction.
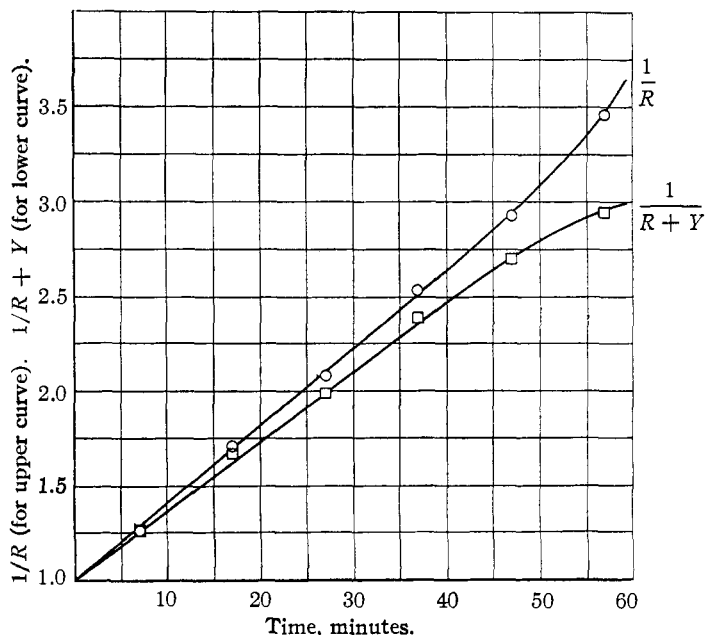

Fig. 1.—Decomposition of α-methoxystyrene at 260.0°.

In order to be able to determine the best values of k_1 and k_2 using all the data for a run at a given temperature it seemed desirable to express R and X in a power series such that the series would be convergent and have a definite finite limit for all values of the variable. This was accomplished in the following way. Introducing the new variable V defined by the equation

$$V = u/(1 + u) \qquad (16)$$

we see that $V = 0$ for $u = 0$ and that $V < 1$ for all finite values of u (or t). On substitution, the fundamental equations (7) and (8) become

$$(1 - V)^2 \, dR/dV = -R^2 - cRX \qquad (17)$$
$$(1 - V)^2 \, dX/dV = R^2 - cRX \qquad (18)$$

Applying Maclaurin's theorem, we can express R and X and any function of them in a power series in V. We obtain

$$R = 1 - V - \frac{c}{2} V^2 + \frac{c^2}{6} V^3 + \frac{c^2}{3} \left(1 - \frac{c}{8} \right) V^4 +$$
$$\frac{17}{60} c^2 \left(1 - \frac{12}{17} c + \frac{c^2}{34} \right) V^5 + \dots \qquad (19)$$

$$X = V - \frac{c}{2} V^2 - \frac{2}{3} c \left(1 - \frac{c}{4}\right) V^3 - \frac{c}{2} \left(1 - c + \frac{c^2}{12}\right) V^4 -$$
$$\frac{2}{5} c \left(1 - \frac{47}{24} c + \frac{7}{12} c^2 - \frac{c^3}{48}\right) V^5 \dots \qquad (20)$$

$$Y = \frac{c}{2} V^2 + \frac{c}{3} \left(1 - \frac{c}{2}\right) V^3 + \frac{c}{4} \left(1 - \frac{5}{3} c + \frac{c^2}{6}\right) V^4 +$$
$$\frac{c}{5} \left(1 - \frac{8}{3} c + \frac{13}{12} c^2 - \frac{c^3}{24}\right) V^5 \dots \qquad (21)$$

$$X + Y = \frac{1 - R + X}{2} = V - \frac{c}{3} V^3 - \frac{c}{4} \left(1 - \frac{c}{3}\right) V^4 +$$
$$\frac{c}{5} \left(1 - \frac{5}{4} c + \frac{1}{12} c^2\right) V^5 \qquad (22)$$

The greatest value of V met with in our experiments was about two-thirds. Moreover, the value of c was found to be of the order of one-eighth. Accordingly we proceeded as follows. Assuming an approximate value of c and using the experimentally determined values of X and Y for a given
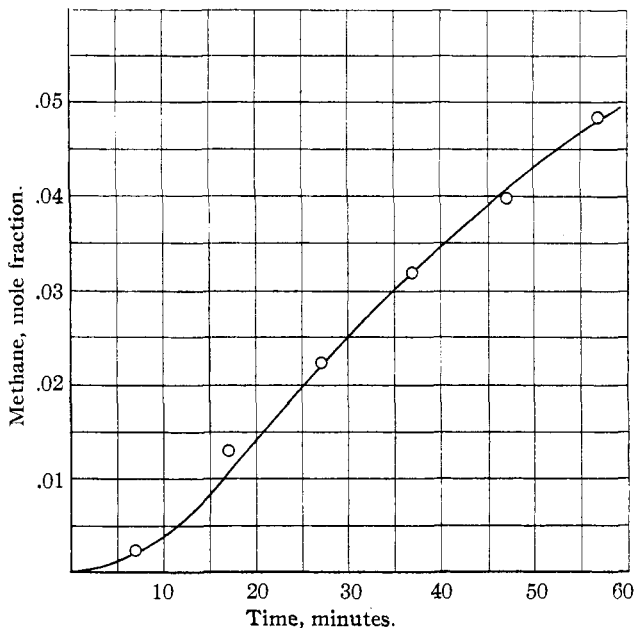

Fig. 2.—Condensation reaction at 260.0°.

time t, an approximate value of V was easily calculated by means of equation (22). Substituting this value of V in equation (19), a more accurate value of c was determined. Using this value of c in equation (22), there resulted a more accurate value of V and on substitution once more in equation (19), we obtained a final value of c. This procedure was gone through for all the data of a run at a given temperature. From the values of V thus obtained for the various times t, equation (16) gave the cor-

responding values of u and hence the values of k_1 (equation (5)).   In Table I are given the results of these calculations applied to the data obtained at 260°.

TABLE I

260°

t (corr.), min.	R	X	Y	c	V	u	k_1	k_2
7	0.7963	0.1989	0.0024	[0.100]	0.2017	0.2527	0.0361	
17	.5888	.3850	.0131	.123	.4017	.6714	.0395	
27	.4800	.4752	.0224	.124	.5051	1.021	.0378	
37	.3950	.5414	.0318	.126	5851	1.410	.0381	
47	.3413	.5791	.0397	.133	.6342	1.734	.0369	
57	.2989	.6134	.0484	.122	.6760	2.086	.0366	
				Av. 0.126			0.0375	0.00473

As additional evidence in regard to the correctness of our fundamental equations, we give in Table II the values of R and of Y calculated by means of equations (19) and (21), assuming $k_1 = 0.0375$; $c = 0.126$ and $k_2 =$

TABLE II

CALCULATION OF R AND Y AT 260°

$k_1 = 0.0375$; $c = 0.126$; $k_2 = 0.00473$

t, min.	7	17	27	37	47	57
R, obs.	0.7963	0.5888	0.4800	0.3950	0.3413	0.2989
R, calcd.	.7894	.6015	.4817	.3989	.3383	.2920
Y, obs.	.0024	.0131	.0224	.0318	.0397	.0484
Y, calcd.	.0031	.0126	.0231	.0330	.0418	.0496

TABLE III

REACTION AT 249.5°

t (corr.), min.	R	X	Y	c	k_1	k_2
12	0.8284	0.1676	0.0020	0.138	0.0170	
27	.6799	.3055	.0073	.120	.0170	
42	.5610	.4192	.0099	[.067]	.0182	
57	.4567	.4981	.0226	.108	.0197	
72	.4123	.5317	.0280	.122	.0184	
87	.3350	.5914	.0368	.125	.0207	
102	.3007	.6117	.0438	.135	.0201	
			Av.	0.125	0.0187	0.00234

TABLE IV

REACTION AT 235.6°

t (corr.), min.	R	X	Y	c	k_1	k_2
27	0.8231	0.1725	0.0022	0.132	0.00785	
57	.6983	.2893	.0062	.114	.00740	
87	.5613	.4117	.0135	.106	.00864	
117	.4473	.5011	.0258	.132	.00982	
147	.4041	.5317	.0321	.144	.00914	
177	.3561	.5701	.0369	.137	.00918	
			Av.	0.128	0.00867	0.00111

0.00473.   The agreement between calculated and observed values is very satisfactory.

Tables III and IV give the results obtained from the experiments at 249.5 and 235.6°.

Experiments at 222.8°C.—At the temperature 222.8° a run was made starting with approximately equivalent amounts of α-methoxystyrene and propiophenone.   Representing by a the mole fraction of α-methoxystyrene at the beginning of the reaction, we obtain as solutions in series of equations (17) and (18)

$$R/a = 1 - [a + (1 - a)c]V - \left[a - a^2 + \left(\frac{2 - 5a + 4a^2}{2}\right)c - \left(\frac{1 - a}{2}\right)c^2\right]V^2 - \left[a(1 - a)^2 + (1 - 4a + 6a^2 - 3a^3)c - \frac{(6 - 13a + 14a^2 - 6a^3)}{6}c^2 + \frac{(1 + a - 4a^2 + 2a^3)}{6}c^3\right]V^3 + \ldots$$

$$X/a = \frac{1 - a}{a} + [a - (1 - a)c]V + \left[a - a^2 - \left(\frac{2 - a}{2}\right)c + \left(\frac{1 - a}{2}\right)c^2\right]V^2 + \left[a(1 - a)^2 - \left(\frac{3 - 4a^2 + 3a^3}{3}\right)c + \left(\frac{6 - 5a + 2a^2 - 2a^3}{6}\right)c^2 - \left(\frac{1 + a - 4a^2 + 2a^3}{6}\right)c^3\right]V^3 + \ldots$$

$$Y/a = (1 - a)cV + \left[\left(\frac{2 - 3a + 2a^2}{3}\right)c - \left(\frac{1 - a}{2}\right)c^2\right]V^2 + \left[\left(\frac{3 - 6a + 7a^2 - 3a^3}{3}\right)c - \left(\frac{6 - 9a + 8a^2 - 4a^3}{6}\right)c^2 + \left(\frac{1 + a - 4a^2 + 2a^3}{6}\right)c^3\right]V^3 + \ldots$$

Unfortunately these series do not converge rapidly when the value of V is as great as one-half so that the use of the first four terms of each series gives only an approximate value of the function represented.   Moreover, the reactions do not seem to go so smoothly at 222.8° as at the higher temperatures.   Nevertheless, it was possible to get some idea as to the magnitude of k_1 and k_2.   The experimental data are given in Table V.   It will perhaps be sufficient to state that these data lead to values of k_1 lying between 0.004 and 0.005 and a value of k_2 in the neighborhood of 0.0005.   Table VI contains a summary of the results at the three higher temperatures.

TABLE V
REACTION AT 222.8°

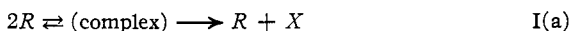| t (corr.), min.	0	57	117	177	237	297
R	0.4864	0.4377	0.3797	0.3152	0.2825	0.2653
X	.5136	.5549	.6013	.6514	.6727	.6855
Y	.0000	.0037	.0095	.0167	.0224	.0246

TABLE VI

t, °C.	260	249.5	235.6
$k_1 \times 10^3$	37.5	18.7	8.67
$k_2 \times 10^3$	4.73	2.34	1.11

Energy of Activation.—The quantity A in the Arrhenius equation

$$d \log_e k/dT = A/RT^2$$

is usually interpreted as the energy of activation. This equation in integrated form is

$$A = \frac{2.303\, RT_1 T_2}{T_2 - T_1}\left(\log_{10} \frac{k_{T_2}}{k_{T_1}}\right)$$

Since the ratio of k_2 to k_1 has been found to be practically constant from 235 to 260°, it follows that both reactions have the same energy of activation. From the values of k_1 at 260 and 249.5°, we find $A = 36,700$ calories; from the data at 260 and 235.6° we find $A = 32,300$ calories. The energy of activation is thus found to be about 34,000 calories.

Kinetic Mechanism of Rearrangement.—Since Reaction I is found to be of the second order with respect to R, we may suppose that when two molecules of R encounter each other under appropriate energy conditions, an activation complex is formed which, on the one hand, can break down re-forming two molecules of R and, on the other hand, can break down forming either one molecule of R and one molecule of X or two molecules of X. If the rate at which the complex breaks up forming $R + X$ (or $2X$) is not too great, the concentration of the complex will be maintained at its equilibrium value with respect to R. Under these circumstances the velocity of Reaction I will be proportional to the square of the concentration of R. Reaction I will still be one of the second order even if the complex is not in equilibrium with R but decomposes solely into $R + X$ (or $2X$), provided that the concentration, C, of the complex is always so minute that dC/dt is negligibly small in comparison with the rate of formation of the complex or its rate of decomposition. Reaction I may then be represented by the scheme

$$2R \rightleftarrows \text{(complex)} \longrightarrow R + X \qquad\qquad \text{I(a)}$$

or

$$2R \rightleftarrows \text{(complex)} \longrightarrow 2X \qquad\qquad \text{I(b)}$$

Reaction II is a typical bimolecular process given by the scheme

$$R + X \rightleftarrows \text{(complex)} \longrightarrow Y + Z \qquad\qquad \text{II}$$
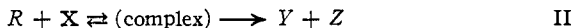
Summary

1.   The rearrangement of α-methoxystyrene to propiophenone is accompanied by an unusual type of side reaction in which the methoxystyrene and propiophenone react to form methane and 1,2-dibenzoylpropane.

2.   The kinetics of these reactions was investigated at the temperatures, 260, 249.5, 235.6 and 222.8°.

3.   Both reactions were found to be of the second order.

4.   The differential equations describing the reactions were integrated in the form of infinite series.

5.   The ratio of k_2 to k_1 remains virtually unchanged in the range 235–260°.

6. Both reactions have equal energies of activation, the value of which is 34,000 calories.

Studies on Oxidation–Reduction. XIX. Aposafranines

BY ROBERT D. STIEHLER[1] AND W. MANSFIELD CLARK

In the previous paper[2] of this series there were reported the equilibrium potentials of oxidation–reduction systems the oxidants of which are simple safranines. Data for several other azine systems, which may be designated by the names of the following oxidants, are now reported.
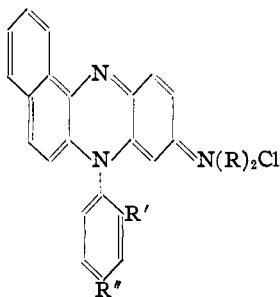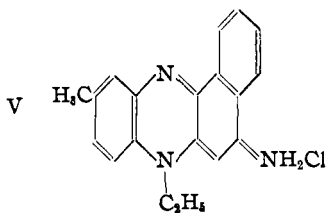

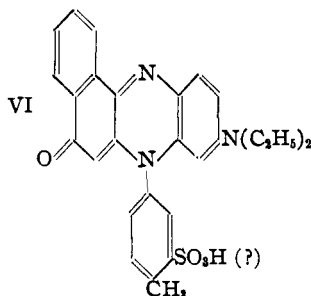I   Neutral blue (Rowe 832): R = CH$_3$; R' = H; R" = H

II   Isorosinduline No. 1: R = C$_2$H$_5$; R' = H; R" = H

III Isorosinduline No. 2: R = C$_2$H$_5$; R' = H; R" = CH$_3$

IV   Isorosinduline No. 3: R = C$_2$H$_5$; R' = CH$_3$; R" = H

Induline Scarlet (Rowe 827)

Sulfonated Rosindone

We are indebted to Dr. H. A. Lubs and Dr. P. W. Carleton of E. I du Pont de Nemours and Company for authentic samples of all the dyes except induline scarlet

The rosindone is particularly interesting because it provided material with which to study the so-called "concentration effect" discussed in the previous paper. The results of this study support the suggestion of

(1) R. D. Stiehler presented the details of this study in a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University.

(2) Stiehler, Chen and Clark, THIS JOURNAL, **55**, 891 (1933).