The Alkaline Hydrolysis of Yellow Azomethine Dyes

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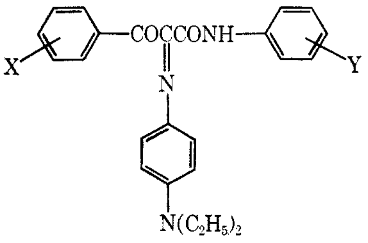
The reaction of substituted 1-{N-[*p*-(diethylamino)phenyl]-2-phenylglyoxylimidoyl}formanilides (I) with sodium hydroxide in 50 vol % aqueous acetone was studied. The decomposition is first order in dye but not in hydroxide unless dilute. Instead, its reciprocal gives a straight line when plotted against $1/[OH^-]$. This, together with other evidence such as substituent effects, indicates that the decomposition is preceded by rapid establishment of an equilibrium. The equilibrium constant depends largely on the substituent in the anilide ring, whereas the rate of decomposition appears to be affected only by the substituent in the benzoyl group. These observations are consistent with the following two mechanisms. One proceeds through an anilide anion which attacks an adjacent water molecule to form a cyclic transition state that breaks down with the formation of the substituted benzoic acid. The other mechanism involves the rate-determining attack of hydroxide ion at the keto carbon atom of the undissociated substrate.

The fugitivity of color-photographic image dyes has long attracted the interest of photographic chemists. Efforts have been made to clarify the aspects of the reaction of these dyes in the bulk phase.[1] Recently, De Hoffmann and Bruylants[2] have made a kinetic study of the acid hydrolysis of a series of 1-{N-[*p*-(dimethylamino)phenyl]-2-phenylglyoxylimidoyl}formanilides, which are widely used as image dyes in color photography. They tried the alkaline hydrolysis too, but "encountered a very serious difficulty."[2] Our preliminary study[3] with analogous 1-{N-[*p*-(diethylamino)phenyl]-2-phenylglyoxylimidoyl}formanilides I has suggested a remarkable difference of the aspects of these two reactions, and this has conducted us to a more detailed study of the alkaline hydrolysis of I.



I

Results and Discussion

All the measurements were carried out in 50 vol % aqueous acetone unless otherwise specified. The logarithm of the absorbance of the dye solution decreases linearly with time, and the slope is independent of the initial dye concentration, indicating that the reaction is first order in dye. It is not first order in hydroxide, however, and at higher alkali concentration the rate rapidly tends to converge to a limiting value specific to each dye. The relationship is illustrated in Figure 1.

TABLE I

APPARENT RATES OF FADING OF I AT 25.0°, $[OH^-] = 0.026\ M$

Compd no.	X	Y	Log *k*
1	H	H	−3.31
2	H	*p*-OCH_3	−3.20
3	H	*p*-Cl	−3.28
4	H	*m*-CF_3	−3.43
5	H	*m*-Br	−3.32
6	H	*o*-OCH_3	−3.32
7	H	2-CH_3-6-OCH_3	−3.22
8	H	2,6-$(CH_3)_2$	−3.23
9	*p*-NH_2	H	*a*
10	*p*-OCH_3	H	−4.23
11	*p*-CH_3	H	−3.86
12	*m*-CH_3	H	−3.34
13	*p*-F	H	−3.30
14	*p*-Cl	H	−1.0
15	*m*-NO_2	H	*b*
16	*o*-OCH_3	H	−3.69
17	*o*-CH_3	H	−3.31
18	*o*-F	H	−0.4
19	*o*-Cl	H	0
20	2,4,6-$(CH_3)_3$	H	*a*
21	*c*	H	−4.43
22[d]	H	H	−3.17
23[e]	H	H	−3.19

[a] Too slow reaction. [b] Too rapid reaction. [c] $(CH_3)_3CCO$– instead of X–C_6H_4CO–. [d] –$N(C_2H_5)(CH_2CH_2OH)$ instead of –$N(C_2H_5)_2$). [e] –$C_6H_3(2\text{-}CH_3)[4\text{-}N(C_2H_5)_2]$ instead of –$C_6H_4 \cdot [p\text{-}N(C_2H_5)_2]$.

Table I lists values of the rate constants, $k = -[(1/A)(dA/dt)]$, where A is the absorbance at the wavelength of the maximum visible absorption (λ_{max}) of the original dye solution and t is time in seconds, at a sufficiently low concentration of sodium hydroxide (0.026 *M*) where the rate is almost a linear function of the hydroxide concentration. The observed rate appears to be affected neither by substituents in the anilide ring nor by modification of the *p*-diethylaminophenylimino moiety but by substituents in the benzoyl group with a Hammett ρ value[4] exceeding 3. This suggests that the rate-determining reaction occurs at a site close to the benzoyl group, and hence one may reasonably expect the hydrolytic cleavage of the benzoyl–iminomethyl bond. Indeed, *m*-nitrobenzoic acid was the sole isolable product of the hydrolysis of the corresponding dye. Similarly, aqueous sodium hydroxide converted 2-benzoyl-2-chloroacetanilide into benzoic acid and 2-chloroacetanilide. It should be noted that the acid hydrolysis of these dyes which results in the formation of α,β-diketonanilides is markedly retarded by introduction of a 2-methyl group in the 4-diethylaminophenyl moiety,[5] whereas it is

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(1) *E.g.*, R. L. Reeves and L. K. J. Tong, *J. Amer. Chem. Soc.*, **84**, 2050 (1962).

(2) E. De Hoffmann and A. Bruylants, *Bull. Soc. Chim. Belg.*, **75**, 91 (1966).

(3) K. Sano, *Tetrahedron Lett.*, 3203 (1968).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184.

(5) Our unpublished work.

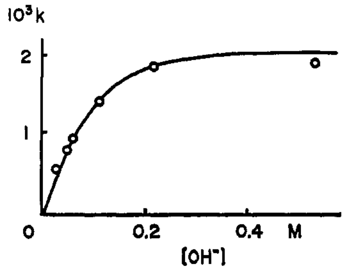

Figure 1.—Fading rate of **1** at various concentrations of sodium hydroxide at 25.0°.

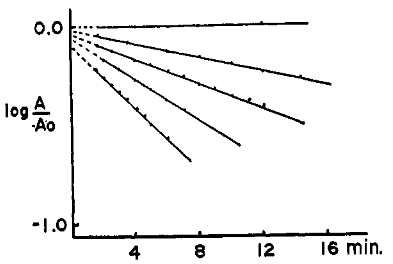

Figure 2.—Plot of log A for **23** against time at various concentrations of sodium hydroxide at 25.0°. The absorbances were measured at 455 mμ.

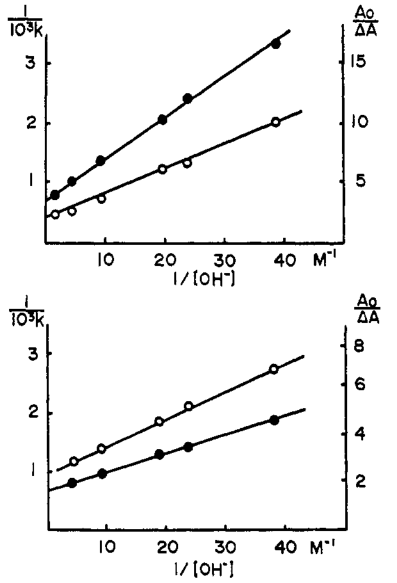

Figure 3.—Fading rate and $A_0/\Delta A$ of **1** (upper) and **4** (lower) at 25.0° as functions of $1/[OH^-]$: ○, $1/k$; ●, $A_0/\Delta A$. In both cases the absorbances were measured at 440 mμ.

affected only slightly by substituents in the benzoyl and anilide rings.[2]

The dye extinction extrapolated to $t = 0$ does not assume a constant value but decreases with increasing alkali concentration, and this decrease again tends to converge to a value specific to each dye (Figure 2). This decrease appears to parallel the deviation of the rate from linearity, and indeed the reciprocal of the fractional decrease ($A_0/\Delta A$, where $A_0 = A_{[OH^-] = 0, t = 0}$ and $\Delta A = A_0 - A_{t = 0}$) and that of k gives two straight lines of an identical slope–intercept ratio when plotted against $1/[OH^-]$ (Figure 3).

The initial dropping of the extinction is too rapid to be followed. The decrease of the extinction extrapolated to $1/[OH^-] = 0$ varies within the range of 6–40% of the original extinction A_0 (at the λ_{max} of the original dye solution), depending on the dye structure. This range and the decrease itself is too large to be accounted for in terms of the change of the electrolyte concentration. Variation of acetone–water ratio from 0.5 to 2.0 brought about a considerable change of the fading rate of **9**, but the ratio $A_0/\Delta A$ remained unchanged as illustrated in Figure 4. Obviously water is not playing an important role in the equilibration step.

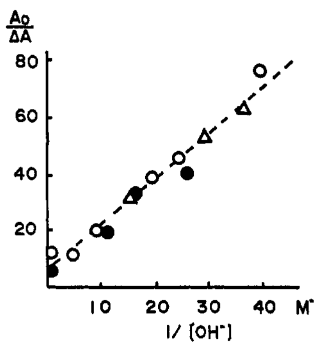

Figure 4.—Effect of solvent composition on $A_0/\Delta A$ of **9** at 25.0°; acetone–water ratio; ○, 2.0; △, 1.0; ●, 0.5. The absorbances were measured at 430 mμ.

The ultraviolet and visible absorption spectra of the dye solutions in the presence and absence of sodium hydroxide differ slightly. Compound **9** for example shows peaks at 341 mμ (ε 26,600) and 437 (19,600) in 1:1 (in volume) ethanol–water, and at 340 (24,700) and 434 (14,200) in 1:1 ethanol–1 N aqueous sodium hydroxide mixture. Although the difference is small when we consider the possible marked difference of the electronic states, the occurrence of a second species is implied. Rapid equilibration prior to hydrolysis was observed in the acid hydrolysis of analogous dyes too, but in this case the protonated species was colorless.[2]

SCHEME I

$$\text{dye} \underset{\underset{\text{fast}}{k_2}}{\overset{k_1[\text{OH}^-]}{\rightleftharpoons}} \text{dye}' \xrightarrow[\text{slow}]{k_3} \text{product}$$

$$\frac{1}{k} = \frac{1}{k_3} + \frac{k_3}{k_1k_3[\text{OH}^-]} \qquad (1)[6]$$

$$\frac{A_0}{\Delta A} = \frac{\epsilon_1}{\epsilon_1 - \epsilon_2}\left(1 + \frac{k_2}{k_1[\text{OH}^-]}\right) \qquad (2)[6]$$

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(6) These equations were obtained in the following way.

$$k = -\frac{1}{A}\frac{dA}{dt} = \frac{1}{\epsilon_1[\text{dye}] + \epsilon_2[\text{dye}'])}\frac{d(\epsilon_1[\text{dye}] + \epsilon_2[\text{dye}'])}{dt}$$

Since $[\text{dye}'] \simeq k_1[\text{OH}^-][\text{dye}]/k_2$, and $[\text{OH}^-]$ is in large excess

$$k = -\frac{1}{[\text{dye}]}\frac{d[\text{dye}]}{dt}$$

According to Scheme I

$$-\frac{d([\text{dye}] + [\text{dye}'])}{dt} = k_3[\text{dye}]$$

Substitution of $[\text{dye}']$ by $k_1[\text{OH}^-][\text{dye}]/k_2$ gives eq 1. Equation 3 is obtained from

$$-\frac{d([\text{dye}] + [\text{dye}'])}{dt} = k_4[\text{OH}^-][\text{dye}]$$

in an analogous way. At the extrapolated (hypothetical) zero time when the equilibration is complete but no decomposition has started

$$\frac{A_0}{\Delta A} = \frac{\epsilon_1([\text{dye}] + [\text{dye}'])}{\epsilon_1([\text{dye}] + [\text{dye}']) - (\epsilon_1[\text{dye}] + \epsilon_2[\text{dye}])} = \frac{\epsilon_1[\text{dye}'](1 + k_2/k_1[\text{OH}^-])}{\epsilon_1[\text{dye}'] - \epsilon_2[\text{dye}']}$$

which is identical with eq 2.

SCHEME II

$$\begin{tikzcd} \text{dye} \arrow[r, shift left, "k_1[OH^-]"] \arrow[d, "k_4[OH^-]"] & \text{dye}' \arrow[l, shift left, "k_2" below, "\text{fast}" below=8pt] \\ \text{product} & \end{tikzcd}$$

$$\frac{1}{k} = \frac{k_1}{k_2k_4} + \frac{1}{k_4[OH^-]} \qquad (3)^6$$

$$\frac{A_0}{\Delta A} = \frac{\epsilon_1}{\epsilon_1 - \epsilon_2}\left(1 + \frac{k_2}{k_1[OH^-]}\right) \qquad \text{(same as eq 2)}$$

TABLE II

RATE AND EQUILIBRIUM CONSTANTS AT 25.0°, CALCULATED ON SCHEMES I AND II

Compd no.	10^3k_3, sec^{-1}	10^3k_4, sec^{-1}	k_1/k_2[a]
1	3.0	23	7.5
2	4.3	24	5.4
3	1.7	28	16
4	1.0	22	21
5	1.3	29	22
6	4.5	20	4.5
7	2.5	31	13
8	2.6	28	11
9	b	b	2.4[c]
10	0.43	2.6	6.0
11	1.1	6.1	5.5
12	2.5	21	8.6
13	5.0	49	9.7
16	2.0	8.5	4.2
17	3.6	22	6.2
20	b	b	16[c]
21	0.38	2.1	5.3
22	3.2	33	10
23	5.0	28	5.6

[a] Determined from $1/k$ *vs.* $1/[OH^-]$ curves unless otherwise indicated. The two schemes lead to the identical k_1/k_2 values. [b] The reaction was too slow for the rate measurement. [c] Determined from $A_0/\Delta A$ *vs.* $1/[OH^-]$ curves.

The features discussed so far lead to the following two possibilities, namely a consecutive (Scheme I) and a parallel (Scheme II) mechanism.

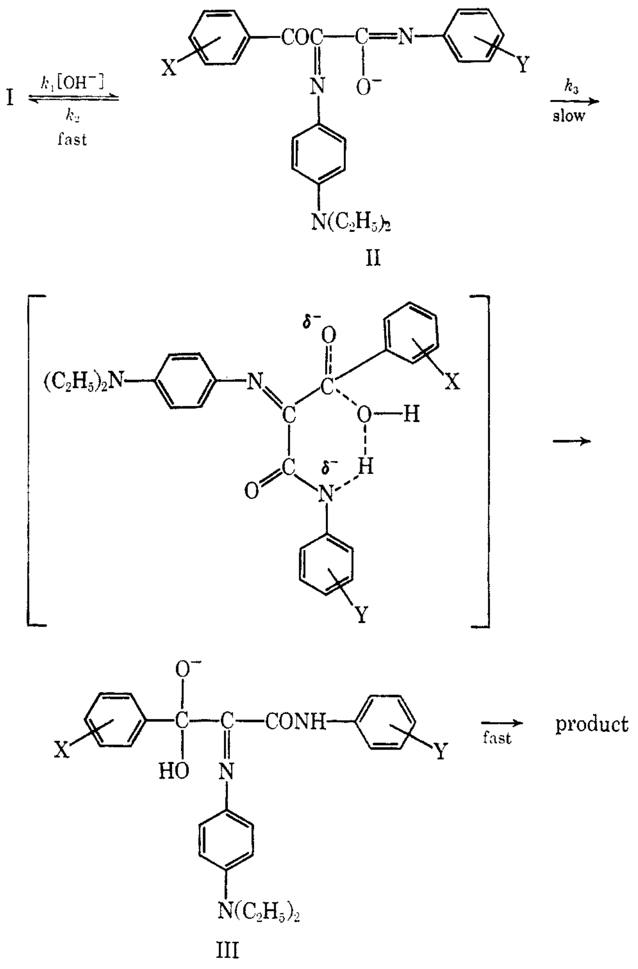
Here, ϵ_1 and ϵ_2 denote the molar absorptivities of dye and dye′ at the λ_{max} of the original dye solution, respectively. The expression "product" does not necessarily mean the final decomposition product.

In Table II are summarized the rate and equilibrium constants calculated on these schemes. Most of the equilibrium constants have been calculated from $1/k$ curves and not from $A_0/\Delta A$ curves since the latter seemed to be subject to greater experimental error at low hydroxide concentration where ΔA's are considerably smaller.

The data cited in this table can be interpreted by either of the two schemes. The equilibrium constant k_1/k_2 is more susceptible to Y substituent effect than to X substituent effect and to modification of the *p*-diethylaminophenyl moiety. In addition, the compounds with sterically crowded keto groups such as **16**, **17**, and **21** (with the exception of **20**) exhibit no extraordinary k_1/k_2 value. These facts indicate that the equilibration reaction is not taking place in the vicinity of the keto group in contrast to the decomposition reaction, and hence that dye′ is formed by dissociation of the anilide hydrogen.

Thus, Scheme I proposes a mechanism involving the attack of the anilide anion on an adjacent water molecule with simultaneous attack by oxygen on the carbonyl group which leads to the fission of the benzoyliminomethyl bond (Scheme III).

SCHEME III

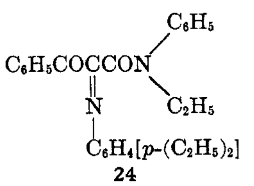


Since k_3 involves proton transfer to anilide anion one may reasonably expect a good Brønsted relation between k_3 and k_2/k_1.[7] This is in fact observed (Figure 5) and $\beta = 0.8$ suggesting that the protonation is nearly complete at the transition state.

The rate constant k_3 also involves the attack by a partially formed hydroxide ion on the carbonyl group. Accordingly the Hammett ρ value is expected to be positive with respect to X whereas it should be negative with respect to Y. Figure 6 shows reasonable ρ values of +3.0 and −0.9, respectively.

At the base concentration cited in Table I, k_3 was approximately $k_1k_3[OH^-]/k_2$. Since k_3 tends to decrease as k_1/k_2 increases, the seemingly small effect of Y on k must have been the consequence of this compensation effect.

The N-ethyl derivative **24**, which is incapable of forming an anion, showed no initial rapid dropping of



$C_6H_5COC(=N\text{-}C_6H_4[p\text{-}(C_2H_5)_2])CON(C_6H_5)C_2H_5$

24

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[7] J. N. Brønsted and K. J. Pedersen, *Z. Phys. Chem.*, **108**, 185 (1924).

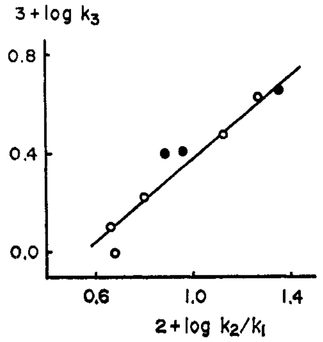


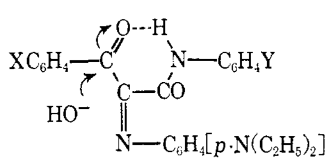
Figure 5.—The Brønsted relationship between k_3 and k_2/k_1, temperature = 25.0°. ○, **1–5**; ●, **6–8**.

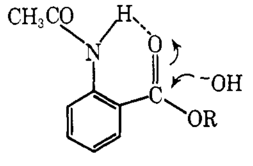
extinction. The remarkable resistance of this compound toward hydrolysis is consistent with the above-mentioned reaction pathway.

According to Scheme II, k_4 is correlated with X by a large Hammett ρ value of $+3.6$ (Figure 7). This suggests the rate-determining attack of hydroxide ion on the carbonyl carbon which results in the formation of the intermediate III and in the subsequent cleavage of the benzoyl–iminomethyl bond.

$$\begin{tikzcd} \mathrm{I} \arrow[r, shift left, "k_1[\mathrm{OH}^-]"] \arrow[d, "k_4[\mathrm{OH}^-]\ (\mathrm{slow})"] & \mathrm{II} \arrow[l, shift left, "k_2"] \\ \lbrack\mathrm{III}\rbrack \arrow[r, "\mathrm{fast}"'] & \text{product} \end{tikzcd}$$

The extremely slow reaction of **24** can be interpreted in terms of the absence of the acceleration by intramolecular hydrogen bonding. At present we cannot decide which mechanism is really operating. An alkaline hydrolysis study of *o*-acetaminobenzoic ester IV, which is now under progress, might offer some information on the possibility of the latter mechanism. It should be noted that the substrates can exist in conformational isomers at the imino function. Since we have no knowledge of the geometry of the species undergoing hydrolysis, we may have been discussing the composite constants of the two possible isomers.





IV

It is surprising that 1-{N-[*p*-(diethylamino)phenyl]-2-phenylglyoxylimidoyl]formyl group is so strongly electron withdrawing despite that the conjugation system is expected to increase the electron density of the central carbon atom[8] or that of the keto oxygen.[9] The large values of k_1/k_2 of 2,6-disubstituted anilides are worth noting. The 2′,6′-disubstituted benzoylacetanilides have been found to have smaller acid dissociation constants of the active methylene group than the corresponding 2′,4′-disubstituted ones.[10] Presumably the liberation of the anilide hydrogen relieves the steric strain.

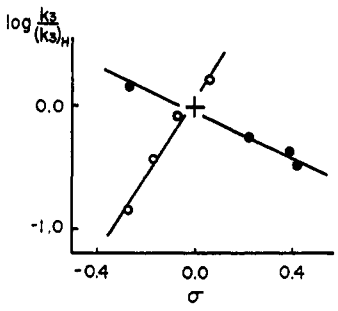


Figure 6.—The Hammett plots of k_3 against X (○) and Y (●), temperature = 25.0°.

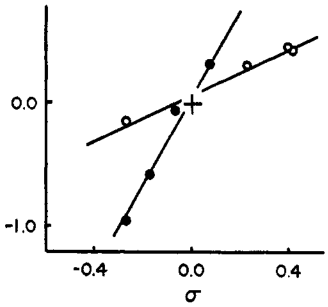


Figure 7.—The Hammett plots of k_1/k_2 (○) and k_4 (●) against Y and X, respectively, temperature = 25.0°; abscissa, log k_1/k_2 − log $(k_1/k_2)_\mathrm{H}$ and log $k_4/(k_4)_\mathrm{H}$.

Experimental Section

Rate Measurement.—Solutions of 10^{-4} *M* dye in acetone and 1.0, 0.40, 0.20, 0.10, 0.075 and 0.05 *N* sodium hydroxide in distilled water were prepared. One volume of the dye solution was mixed with one volume of fresh aqueous sodium hydroxide to make 1.92 volumes, and the absorbance was followed in an optical cell thermostated by means of circulating water, using Hitachi EPS-II spectrophotometer.

Hydrolysis of 15.—A 1-g sample of **15** was dissolved in 20 ml of acetone, and to the warmed solution was added 4 ml of 5 *N* aqueous sodium hydroxide. After the solution had become colorless, 12 ml of 1 *N* hydrochloric acid was added. *m*-Nitrobenzoic acid that precipitated was collected, washed with water, and recrystallized from methanol. Identification was made by infrared spectrometry.

Hydrolysis of 2-Benzoyl-2-chloroacetanilide.—A 1-g sample of 2-benzoyl-2-chloroacetanilide was dissolved in 20 ml of 1 *N* sodium hydroxide and was heated on a steam bath for 10 min, during which period 2-chloroacetanilide began to separate. The precipitates were collected, recrystallized from aqueous methanol, and subjected to mixture melting point measurement. The alkaline filtrate was acidified with concentrated hydrochloric acid to separate benzoic acid, which was identified by infrared spectrometry.

Materials. Dyes. General Procedure A.—In a 1-l. three-necked flask equipped with a stirrer was added a solution of 0.04 mol of *p*-amino-N,N-dialkylaniline and 0.02 mol of 2-acylacetanylide dissolved in 300 ml of 2% aqueous sodium hydroxide. To the stirred mixture was added a solution of 0.01 mol of ammonium persulfate in 200 ml of water during 1 hr.

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[8] J. J. Jennen, *Chim. Ind.*, **86**, 400 (1961).

[9] G. H. Brown, J. Figueras, R. J. Gledhill, C. J. Kibler, F. C. McCrossen, S. M. Parmerter, P. W. Vittum, and A. Weissberger, *J. Amer. Chem. Soc.*, **79**, 2919 (1957).

[10] Private communication from Y. Oishi of our laboratory, who reported the p*K* values of 10.16, 9.53, 9.38, and 8.25 for 2′,6′-dimethyl-, 2′,4′-dimethyl, 2′,6′-dichloro-, and 2′,4′-dichloro-2-benzoylacetanilide, respectively, in 60 vol % aqueous ethanol at 25°.

Stirring was continued for another 30 minutes and the precipitates were collected, dried, and recrystallized from ethanol or other suitable solvents.

General Procedure B.—Some of the dyes were prepared by condensation of the acylacetanylide with *p*-nitroso-N,N-dialkylaniline in the same fashion as the procedure of De Hoffmann, *et al.*[11] This procedure was suitable for the components that were unreactive toward oxidized *p*-amino-N,N-dialkylaniline although very cautious purification of the product was necessary in order to avoid contamination with azomethine N-oxide.

Compound **24** did not crystallize from the reaction mixture and was purified by repeated thin layer chromatography on silica gel using 1:4 methanol–benzene mixture. The acetone extract was directly used for the measurement.

Table III lists the melting points and nitrogen analyses of the dyes. Further structural confirmation was given by comparison of the infrared spectra with that of authentic **23** reported by Brown, *et al.*[9]

Most of the benzoylacetanilides were already reported by these authors, and unreported members were prepared in an analogous way.

Registry No.—**1,** 4754-85-2; **2,** 19650-46-5; **3,** 19650-47-6; **4,** 19755-72-7; **5,** 19779-37-4; **6,** 19755-73-8; **7,** 19755-74-9; **8,** 19755-79-4; **9,** 19755-80-7; **10,** 19650-48-7; **11,** 19755-82-9; **12,** 19755-83-0; **13,** 19755-84-1; **14,** 19755-85-2; **15,** 19779-38-5; **16,** 19650-49-8; **17,** 19755-87-4; **18,** 19755-88-5; **19,** 19755-89-6; **20,** 19759-05-8; **21,** 19759-06-9; **22,** 4754-88-5.

TABLE III
MELTING POINTS, SYNTHETIC PROCEDURES, AND ANALYSES OF DYES

Compd no.	Mp, °C	Synthetic procedure	N analysis, % Calcd	Found
1	209	A	10.52	10.38
2	162	A	9.78	10.07
3	192	A	9.66	9.72
4	118	A	8.99	9.14
5	147	A	8.79	8.63
6	149	A	9.78	9.72
7	157	B	9.48	9.51
8	183	B	9.84	9.82
9	203	A	13.52	13.90
10	131	A	9.78	9.53
11	162	A	10.16	10.09
12	182	A	10.16	10.03
13	220	A	10.06	10.17
14	114	A	9.66	9.43
15	139	A	12.61	12.27
16	144	A	9.74	9.79
17	171	A	10.16	10.10
18	207	A	10.06	10.16
19	182	A	9.66	9.55
20	180	B	9.44	9.52
21	119	A	11.07	11.03
22	155	A	10.11	10.19

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[11] E. De Hoffmann and A. Bruylants, *Bull. Soc. Chim. Belg.*, **74**, 609 (1965).

The Conformational Preferences of Sulfur and Oxygen in Hemithioketals[1]

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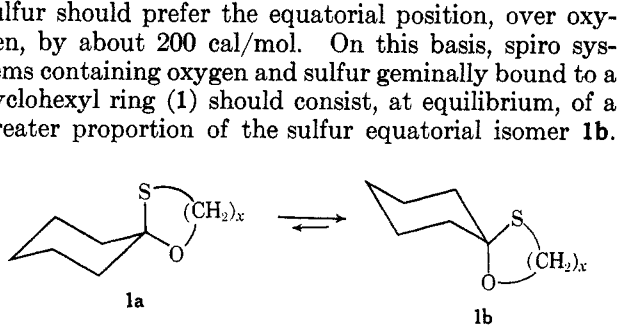
Both second-order catalytic rate constants and isomer ratios at equilibrium for boron trifluoride catalyzed interconversion of the equatorial oxygen and sulfur ethylene hemithioketals of 3,3,5-trimethylcyclohexanone are independent of catalyst concentration in the range of 0.016–0.095 *M* BF_3. Thus no catalyst complex with the hemithioketal forms to a significant extent and the equilibrium constant of 0.285 ± 0.005 favoring the equatorial oxygen species is a true measure of conformational preference in the hemithioketal.

The early conformational analysis studies of divalent sulfur attached to cyclohexyl systems were performed by Chiurdoglu and coworkers.[3] Subsequent studies by Eliel and coworkers,[4,5] using nuclear magnetic resonance suggested the opposite; values of 0.8 kcal/mol for SC_6H_5, 0.7 kcal/mol for SCH_3, and 0.9 kcal/mol for SH were found. Thus, the authors concluded that the nature of the substituent on sulfur (C_6H_5, CH_3, or H) appeared to have little effect on its conformational preference, which was for the equatorial position. Earlier studies on oxygen derivatives had given similar results.

A comparison of the conformational preferences of oxygen ($-\Delta G_{av} \sim 0.6$ kcal/mol) and sulfur ($-\Delta G_{av} \sim 0.8$ kcal/mol) derivatives leads to the prediction that sulfur should prefer the equatorial position, over oxygen, by about 200 cal/mol. On this basis, spiro systems containing oxygen and sulfur geminally bound to a cyclohexyl ring (**1**) should consist, at equilibrium, of a greater proportion of the sulfur equatorial isomer **1b**.



1a **1b**

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[2] Holders of Research Career Development Awards of the National Cancer Institute (M.P.M.) 1K3-CA-10,739 and the National Institute of General Medical Sciences (R.L.S.) 1-K4-GM-10,913.

[3] G. Chiurdoglu, J. Reisse, and M. VanderStichelen Rogier, *Chem. Ind.* (London), 1874 (1961). Interpretation of the infrared and Raman spectra of cyclohexanethiol resulted in the assignment of a conformational free-energy difference ($-\Delta G \equiv G_{ax} - G_{eq}$) of −0.4 kcal/mole to the SH group, a remarkable preference for the axial position.

[4] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[5] (a) E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, 97 (1962); (b) E. L. Eliel and B. P. Thill, *Chem. Ind.* (London), 88 (1963).