

Now

$$pK_{B_1, X} \cong (-1) \log \frac{C_{H_3O^+} C_B}{C_{B_1H^+}}; \quad pK_{B_n, X} \cong (-1) \log \frac{C_{H_3O^+} C_B}{C_{B_nH^+}} \quad (18)$$

Then

$$\log \frac{C_{B_1H^+}}{C_{B_nH^+}} = (\alpha_1 - \alpha_n) \sigma_{1X} + (\beta_1 - \beta_n) \sigma_{RX} \quad (19)$$

Defining

$$K_T = \frac{C_{B_nH^+}}{C_{B_1H^+}} \quad (20)$$

we obtain eq. 21. An example of this type of tauto-

$$\log K_T = (\alpha_n - \alpha_1) \sigma_{1X} + (\beta_n - \beta_1) \sigma_{RX} \quad (21)$$

meric equilibrium is the ionization of a 4-substituted pyrimidine. We hope to discuss this system in a following paper.

Neighboring-Group Effects in the Hydrolysis of 1-Silylpropyl-2-imidazolines

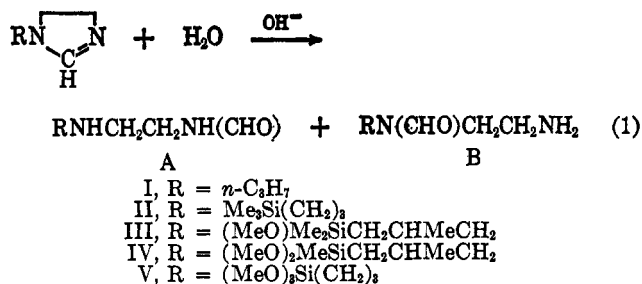
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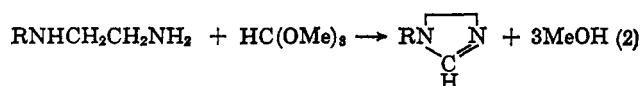
The hydrolysis of the imino bond in a group of 1-(3-silylpropyl)-2-imidazolines was shown to be first order in imidazoline in aqueous alkaline solution. With one exception, the series gave a pseudo-first-order rate constant, $k_{\text{obsd}} = k_A[\text{OH}]/(1 + K[\text{OH}])$. One example, 1-(3-trimethylsilylpropyl)-2-imidazoline (V), gave $k_{\text{obsd}} = (k_A[\text{OH}] + k_B[\text{OH}]^2)/(1 + K[\text{OH}])$. This was interpreted as a neighboring-group interaction with the silyl group of V which assists direct attack of the nucleophile on the free base of V.

Participation of the trimethylsilyl group in the transition state has been invoked to explain the enhanced rate of displacement of chloride from chloromethyltrimethylsilane.¹ The importance of such effects for other organofunctional silicon compounds is largely unknown. The synthesis of 1-(3-silylalkyl)-2-imidazolines provided an opportunity to search for effects of the silyl group during hydrolysis of an imidazoline ring according to eq. 1. The rate-controlling step



for similar reactions in alkaline solution has been pictured as an attack of hydroxide ion on the protonated imino group.² Any interactions between the imidazoline ring and silicon which might facilitate the attack of the nucleophile would then be apparent in the kinetics of the system.

2-Imidazolines were prepared according to eq. 2.³ The products of hydrolysis of compounds II and III were isolated and identified as being mostly A, R = Me₃Si(CH₂)₃ and O_{0.5}Me₂SiCH₂CHMeCH₂, respectively. The other 2-imidazolines were assumed to give analogous products.



Experimental Section

1-(3-Silylalkyl)-2-imidazolines were prepared by a modification of the method reported by Hill and Johnston.³ A mixture of the N-propyl- or N-(silylpropyl)-1,2-ethylenediamine and a 5–10% molar excess of methyl orthoformate was heated in a stainless steel bomb at 180–200° until no further increase in pressure was noted. About 1.5–3 hr. were required to reach a maximum pressure of about 20 atm. In certain cases the reaction became noticeably exothermic (see Table I) before a temperature of 200° was reached. In these examples, although the external heating was discontinued as soon as an exothermic reaction was observed, the temperatures rose well beyond 200°. The products were isolated by vacuum distillation. The results are summarized in Table I. Physical properties and analyses are given in Table II. The infrared spectra of the 2-imidazolines showed a strong absorption at 6.1–6.2 μ (in CCl₄ solution) characteristic of C=N stretching.⁴ They all showed the strong absorption at 229–234 mμ (in isoctane) in the ultraviolet characteristic of 2-imidazolines.⁵

Hydrolysis of 1-(3-Trimethylsilylpropyl)-2-imidazoline

A mixture 10 g. of 1-(3-trimethylsilylpropyl)-2-imidazoline (II) and 10 g. of water was saturated with potassium carbonate. Two layers separated. The aqueous phase was extracted with ether and the extracts were combined with the organic phase. The solution was evaporated. The residue was kept in a vacuum at room temperature for 96 hr. A 93% yield, 10.7 g., of N-[2-(3-trimethylsilylpropylamino)ethyl]formamide [A, R = Me₃Si(CH₂)₃] hydrated with 0.5 mole of water resulted.

The infrared spectrum (in dilute CCl₄ solution) showed a broad single absorption at 3.01, a strong absorption at 5.94 for carbonyl, and a single sharp absorption at 8.01 μ for methyl on silicon. The lack of a doublet in the 3-μ region and the absence of significant absorption in the 6.0–6.3-μ region indicated the absence of significant amounts of primary amine B.

Anal. Calcd. for C₉H₂₃N₂O_{1.5}Si: neut. equiv., 211. Found: neut. equiv., 211.8.

The above formamide (3.22 g.) was treated with 2.46 g. phenylisothiocyanate in 25 ml. of benzene. The benzene solution was mixed with 50 ml. of pentane and the resulting crystals, 3.12 g., 56% yield, were filtered. Recrystallization of the solid from ethanol water and drying gave the phenylthiourea derivative of A [R = Me₃Si(CH₂)₃], m.p. 116.5–118.0°.

(4) F. H. Suydam, *Anal. Chem.*, **35**, 193 (1963). The absorption was shifted by about 30 cm.⁻¹ to lower frequencies than those reported above. This was attributed to the strain in the five-membered ring system.

(5) G. H. Daub, J. L. Riebsomer, R. J. Ferm, and E. L. Martin, *J. Org. Chem.*, **18**, 643 (1953).

(1) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p. 433.

(2) E. H. Cordes and W. P. Jencks, *J. Am. Chem. Soc.*, **85**, 2843 (1963).

(3) A. J. Hill and J. V. Johnston, *ibid.*, **76**, 922 (1954).

TABLE I
THE PREPARATION OF $\text{RN}-\text{CH}=\text{NCH}_2\text{CH}_2$ BY EQ. 2

| Compd. | R | Diamine, moles | Ortho ester, moles | Max. temp., °C. | Time, hr. | % yield |
|--------|---|-------------------|-----------------------|-----------------------|--------------|------------|
| I | $\text{CH}_3\text{CH}_2\text{CH}_2$ | 0.5 | 0.55 | 240 ^a | 1.0 | 70 |
| II | $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{CH}_2$ | 1.0 | 1.1 | 210 | 3 | 75 |
| III | $(\text{MeO})\text{Me}_2\text{SiCH}_2\text{CHMeCH}_2$ | 1.0 | 1.1 | 200 | 3 | 92 |
| IV | $(\text{MeO})_2\text{MeSiCH}_2\text{CHMeCH}_2$ | 5.0 | 5.5 | 260 ^a | 1.5 | 83 |
| V | $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2$ | 5.0 | 5.5 | 225 | 3 | 79 |

^a The reaction was exothermic.

TABLE II
PROPERTIES OF 1-(SILYLALKYL)-2-IMIDAZOLINES

| Compd. | B.p., °C. (mm.) | d^{25} | n_D^{25} | R_D | | Si, % | | Neut. equiv. | |
|--------|--------------------|----------|------------|---------------------|-------|--------|----------|--------------|-------|
| | | | | Calcd. ^a | Found | Calcd. | Found | Calcd. | Found |
| I | 114 (72) | 0.9185 | 1.4690 | 0.304 | 0.303 | | <i>b</i> | 112 | 110.8 |
| II | 129 (16) | 0.8939 | 1.4698 | 0.312 | 0.312 | 15.21 | 15.11 | 184.0 | 185.7 |
| III | 124 (4) | 0.9516 | 1.4687 | 0.294 | 0.292 | 13.09 | 13.13 | 214 | 214.3 |
| IV | 210 (100) | 1.004 | 1.4642 | 0.277 | 0.275 | 12.17 | 12.10 | 230 | 226.0 |
| V | 160 (12) | 1.065 | 1.4575 | 0.258 | 0.256 | 12.06 | 12.15 | 232 | 231.3 |

^a The bond refractions were based on A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leicester, *J. Chem. Soc.*, 514 (1952). ^b *Anal.* Calcd. for $\text{C}_8\text{H}_{12}\text{N}_2$: C, 64.30; H, 10.71. Found: C, 63.95; H, 10.61.

Anal. Calcd. for $\text{C}_{15}\text{H}_{27}\text{N}_3\text{OSSi}$: C, 56.99; H, 8.01; N, 12.46; Si, 8.32. Found: C, 56.92; H, 8.49; N, 12.15; Si, 8.42.

The filtered solution of benzene and pentane was evaporated and the resulting oil was redissolved in ethanol. Addition of a small amount of water caused the precipitation of a semisolid material. This solidified after washing with ether; obtained was 0.32 g., (6% yield) of another crystalline form of the phenylthiourea of A [$\text{R} = \text{Me}_3\text{Si}(\text{CH}_2)_3$]. Two recrystallizations from hexane-benzene gave the pure derivative, m.p. 136.5–138.5°. The melting point was 116.5–137° when mixed with the previously isolated form. Cooling the mixture gave a solid which melted at 133–137°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{27}\text{N}_3\text{OSSi}$: C, 56.99; H, 8.01; N, 12.46. Found: C, 56.86; H, 8.41; N, 12.17.

Hydrolysis of 1-(3-dimethylmethoxysilyl-2-methylpropyl)-2-imidazoline was accomplished by mixing 55.6 g. of the 2-imidazoline with 14.0 ml. of water. The reaction was exothermic. The excess water was removed in a vacuum at room temperature. This gave 72.4 g. of the hydrated amide A ($\text{R} = \text{O}_0.5\text{Me}_2\text{SiCH}_2\text{CHMeCH}_2$). The remaining water was removed from a 31-g. portion of the above mixture at 1.0 mm. at room temperature over a period of 45 hr.: n_D^{25} 1.4875; d^{25} 1.013; R_D 0.284 (calcd. R_D 0.285).

Anal. Calcd. for $\text{C}_{15}\text{H}_{42}\text{N}_4\text{O}_3\text{Si}_2$: Si, 13.40; neut. equiv., 209. Found: Si, 13.36; neut. equiv., 209.

The infrared spectrum (in dilute CCl_4 solution) showed absorptions at 3.05 for SiOH , 5.95 for $\text{C}=\text{O}$, 7.97 for $\text{Me}-\text{Si}$, a broad absorption at 9.5 for SiOSi , and a weak absorption at 11.55 μ (weak) for SiOH . The lack of a doublet in the 3- μ region and the absence of significant absorption in the 6.0–6.3- μ region indicated that the primary amine B was essentially absent.

Kinetic Runs.—The 2-imidazolines were freshly distilled prior to use. Spectroquality isopropyl alcohol was obtained from Matheson Coleman and Bell Co. Buffers in the pH range 8–10 were prepared by addition of 0.1 M HCl or NaOH to 0.1 M disodium phosphate and for the pH range 10–12 by the addition of 0.1 M HCl to 0.1 M trisodium phosphate. The ionic strength of the buffer solutions was adjusted to 0.30 with sodium chloride. For certain experiments the buffered solutions were 10^{-4} M in methyltrimethoxysilane. At 10^{-4} M all of the imidazolines and methyltrimethoxysilane gave clear solutions in the buffer.

The hydrolyses were carried out in the cells of a Cary 14 recording spectrophotometer. The reaction was followed by measuring the decrease of the absorption of the particular imidazoline in the phosphate buffer solution. Beer's law held over the concentration range studied. The values of ϵ_{max} are given in Table III. The maximum absorbance of product during the

TABLE III
ULTRAVIOLET SPECTRA OF $\text{RN}-\text{C}=\text{NCH}_2\text{CH}_2$ IN
AQUEOUS ALKALINE SOLUTION

| R | Maximum absorption, | |
|---|------------------------|-------------------------|
| | $m\mu$ | ϵ_{max} |
| $\text{CH}_3\text{CH}_2\text{CH}_2$ | 234 | 6460 |
| $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{CH}_2$ | 237 | 6300 |
| $(\text{MeO})\text{Me}_2\text{SiCH}_2\text{CHMeCH}_2$ | 235 | 7590 |
| $(\text{MeO})_2\text{MeSiCH}_2\text{CHMeCH}_2$ | 234.5 | 7700 |
| $(\text{MeO})_3\text{MeSiCH}_2\text{CH}_2\text{CH}_2$ | 237.5 | 7860 |

first half life at 230–240 $m\mu$ amounted to 1–3% of the total absorbance and was neglected. The absorbance of the buffer was automatically compensated in the double-beam instrument. All runs were carried out at 25.5°.

From 15–40 μl . of a 0.01 M solution of the imidazoline in isopropyl alcohol was injected into a 3.03-ml. cell containing the buffer at 25.5°. The cell had been previously rinsed several times with the buffer solution. The cell and contents were vigorously shaken and placed in the instrument which had been previously set at the maximum absorbance for the particular imidazoline. The absorbance was then measured at various intervals from the time of mixing. The initial concentrations varied from 5×10^{-5} M to 1.3×10^{-4} M and the absorbance at time zero was estimated by extrapolation. The calculations were based on the first 70% of the reaction during which there was no detectable change in pH.

Results

In aqueous alkaline solution at constant pH the disappearance of imidazoline by eq. 1 was first order. Plots of log absorbance vs. time were linear for at least 70% of the reaction for all examples, and the value of the pseudo-first-order rate constant, k_{obsd} , was independent of the initial concentration of the substrate. The value of k_{obsd} was also independent of the total buffer concentration. This can be seen from Figure 1, which is an amplification of the dependence of k_{obsd} on OH^- in the lower extreme of the pH range studied. The absence of significant intercepts indicated that the reaction was specifically catalyzed by hydroxide ion. In acidic solutions there was no detectable hydrolysis.

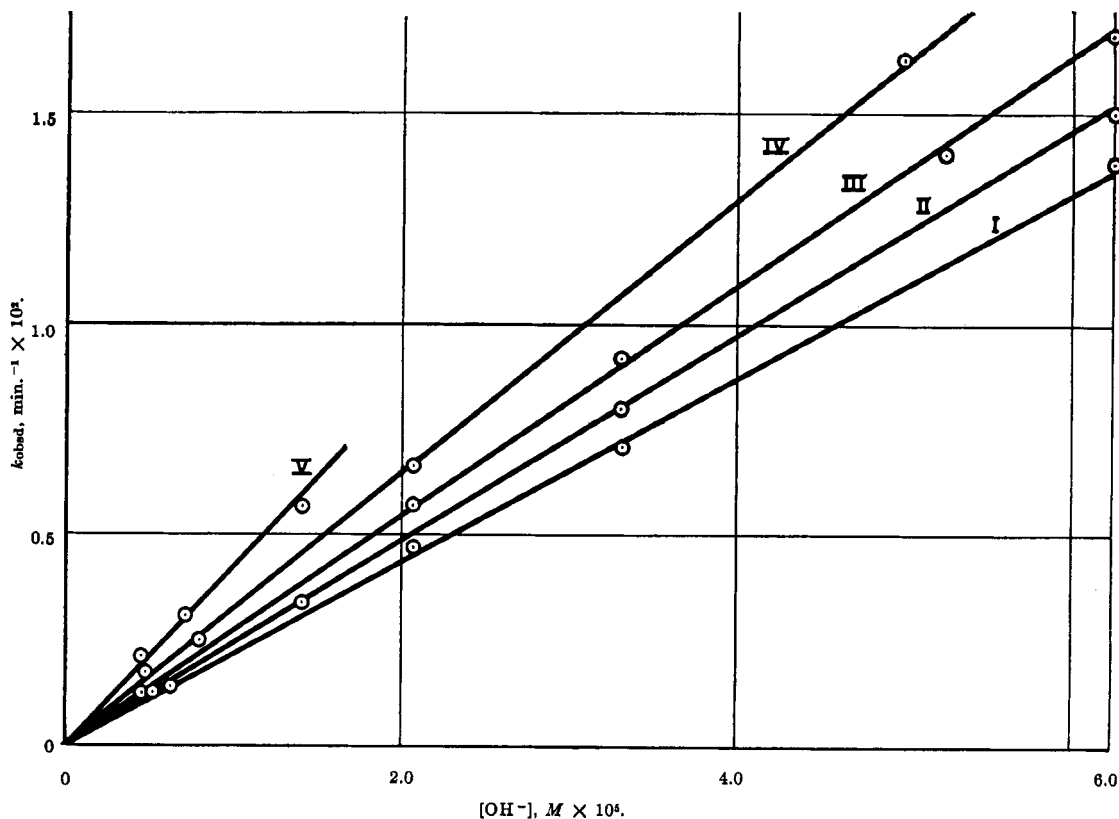


Figure 1.—The dependence of k_{obsd} on OH^- at the lower extreme of OH^- concentration: $[\text{OH}^-] = 10^{\text{pH}-14}$.

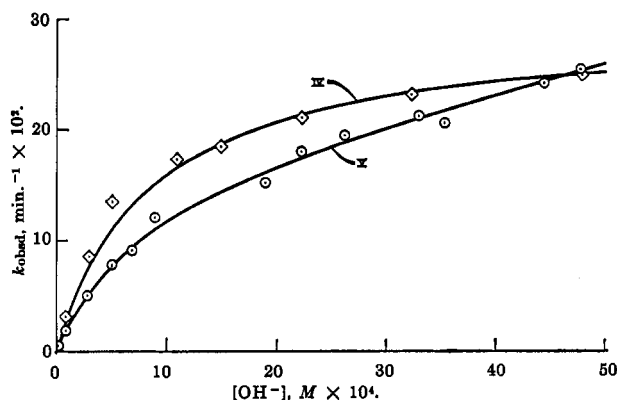


Figure 2.—The dependence of k_{obsd} on OH^- : —◇—, $\text{R} = (\text{MeO})_2\text{MeSiCH}_2\text{CHMeCH}_2$ (IV); —○—, $\text{R} = (\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2$ (V); $[\text{OH}^-] = 10^{\text{pH}-14}$. The data is fitted to eq. 1 for compound IV and to eq. 2 for compound V.

The dependence of k_{obsd} on OH^- concentration for compound V [$\text{R} = (\text{MeO})_3\text{Si}(\text{CH}_2)_3$] was not typical of the other species which showed a dependence resembling that reported by Martin and Parcell for 2-methyl-2-imidazoline.⁶ Figure 2 shows k_{obsd} vs. OH^- concentration for compounds IV and V over the pH range 8.7–11.7. The dependence of k_{obsd} on OH^- for the remaining compounds is shown in Figure 3. With the exception of compound V, k_{obsd} for the hydrolysis of the various 1-(3-silylpropyl)-2-imidazolines was best correlated with hydroxide concentration by

$$k_{\text{obsd}} = k_A[\text{OH}^-]/(1 + K[\text{OH}^-]) \quad (3)$$

where k_A and K are empirical constants. The curves in Figures 2 and 3 are fits of eq. 3 to the data from all compounds but V. Equimolar amounts of methyl-

trimethoxysilane had little or no effect on the rate of hydrolysis of compound II at several different hydroxide concentrations. This indicated the unique behavior of compound V, 1-(3-trimethoxysilylpropyl)-2-imidazoline, was probably due to intramolecular interactions of the hydrolyzed trimethoxysilyl group and the imidazoline ring. The constants from eq. 3 for the imidazolines I–IV are given in Table IV and show little variation with R.

TABLE IV
RATE CONSTANTS FROM EQ. 3 FOR THE
HYDROLYSIS OF COMPOUNDS I–IV AT 25.5°

| Compd. | R | $k_A \times 10^{-3}$ | $K \times 10^{-2}$ |
|--------|---|--------------------------|--------------------|
| | | $M^{-1} \text{min}^{-1}$ | M |
| I | <i>n</i> -Pr | 2.9 | 6.8 |
| II | $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2$ | 2.3 | 6.3 |
| III | $(\text{MeO})\text{Me}_2\text{SiCH}_2\text{CHMeCH}_2$ | 2.8 | 8.7 |
| IV | $(\text{MeO})_2\text{MeSiCH}_2\text{CHMeCH}_2$ | 3.5 | 12.0 |

Instead of approaching a plateau at higher pH as in the other examples, the value of k_{obsd} for compound V continued to increase with increasing hydroxide concentration in a more or less linear fashion. This unique dependence of k_{obsd} on OH^- was described by eq. 4, whose fit is the curve shown in Figure 2 for compound V. The values of the empirical constants in eq. 4 at

$$k_{\text{obsd}} = \frac{k_A[\text{OH}^-] + k_B[\text{OH}^-]^2}{1 + K[\text{OH}^-]} \quad (4)$$

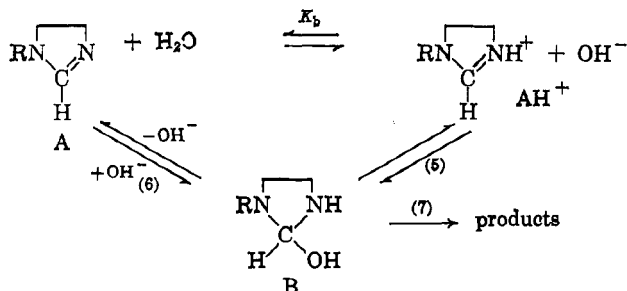
25.5° are $k_A = 2.2 \times 10^2 M^{-1} \text{min}^{-1}$, $k_B = 2.6 \times 10^5 M^{-2} \text{min}^{-1}$, and $K = 12.0 \times 10^2 M^{-1}$.

In examples III, IV, and V the methoxysilyl groups are almost instantly hydrolyzed in dilute aqueous solu-

(6) R. B. Martin and A. Parcell, *J. Am. Chem. Soc.*, **83**, 4830 (1961).

tion⁷ and are undoubtedly in the form of silanols and low molecular weight siloxanes during the hydrolysis of the >C=N- group.

With the exception of compound V, the dependence of k_{obsd} on OH^- resembles that noted by Cordes and Jencks² for the alkaline hydrolysis of certain aliphatic Schiff bases and can be interpreted in similar terms. The rate-determining attack of hydroxide ion on the protonated imidazoline, AH^+ (reaction 5), gives rise to an increasing value of k_{obsd} with increasing hydroxide ion concentration. When further increase in hydroxide ion causes a corresponding decrease in the concentration of AH^+ through the acid-base equilibrium given by K_b , k_{obsd} becomes independent of hydroxide ion. This is seen at $\text{pH} > 11$ for compounds I-IV in Figures 2 and 3. The unusual continuing dependence of k_{obsd} on hydroxide ion concentration in this region is explained by a direct attack of hydroxide ion on the unprotonated form of V (reaction 6) in addition to the usual mode of attack by reaction 5. Instead of forming an anionic form of B, reaction 6 is pictured as giving the carbinolamine directly. This is plausible if the imino nitrogen of A is associated with the solvent through hydrogen bonding.



It is postulated that the carbinolamine (B) achieves a steady state. The observed total imidazoline concentration is given by $[\text{Im}] = [\text{AH}^+] + [\text{A}]$ and the constant $K_b = [\text{AH}^+][\text{OH}^-]/[\text{A}]$. The rate of disappearance of V is then given by

$$-\frac{d[\text{Im}]}{dt} = \frac{k_7(k_5[\text{OH}] + k_6K_b^{-1}[\text{OH}]^2)[\text{Im}]}{(k_{-5} + k_{-6} + k_7)(1 + K_b^{-1}[\text{OH}])} \quad (8)$$

In analogous alkaline hydrolysis of aliphatic Schiff bases, the step corresponding to the reverse of reaction 5 is negligible compared with the corresponding product-forming step, reaction 7.⁸ On this basis it is assumed that $k_7 \gg k_{-5}$. If it is further assumed that $k_7 \gg k_{-6}$, eq. 8 simplifies to

$$-\frac{d[\text{Im}]}{dt} = \frac{(k_5[\text{OH}] + k_6K_b^{-1}[\text{OH}]^2)[\text{Im}]}{1 + K_b^{-1}[\text{OH}]} \quad (9)$$

This agrees with eq. 4 observed for compound V if $k_A = k_5$, $k_B = k_6K_b^{-1}$, and $K = K_b^{-1}$. The rate of attack of hydroxide ion on the protonated imidazoline AH^+ relative to the unprotonated form A would then be given by $k_5/k_6 = K(k_A/k_B) = 1.1$ and indicates that, for compound V, reactions 5 and 6 proceed at nearly equivalent rates. For the remaining compounds, the nucleophile attacks only AH^+ and $k_6 = 0$. Equation 9 then reduces to

$$-\frac{d[\text{Im}]}{dt} = \frac{k_5[\text{OH}][\text{Im}]}{(1 + K_b^{-1}[\text{OH}])} \quad (10)$$

(7) H. Reuther, *Z. anorg. allgem. Chem.*, **272**, 122 (1953).

(8) R. B. Martin, *J. Phys. Chem.*, **68**, 1369 (1964).

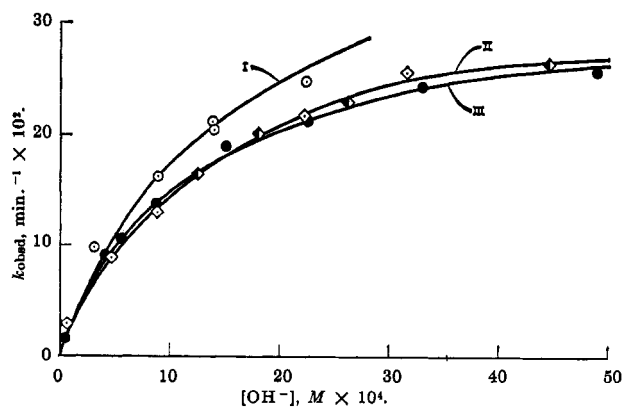
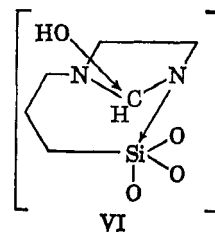


Figure 3.—The dependence of k_{obsd} on OH^- : —○—, $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2$ (I); —◇—, $\text{R} = \text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2$ (II); —●—, II with $(\text{MeO})_3\text{SiMe}$ added; —●—, $\text{R} = (\text{MeO})\text{Me}_2\text{SiCH}_2\text{CHMeCH}_2$; $[\text{OH}] = 10^{\text{pH}-14}$. Data is fitted to eq. 2.

This agrees with eq. 3 if $k_A = k_5$ and $K_b^{-1} = K$. Unfortunately comparisons of K from eq. 3 and 4 with the values of K_b^{-1} determined by titration in aqueous solution are misleading owing to simultaneous hydrolysis of the imidazolines during the titration. Values of K_b^{-1} determined by titration differed by factors of as much as 0.25–0.05 of those found for K .

Conclusions

There appears to be little effect from the presence of silylalkyl groups in examples I-IV and $k_6 = 0$. However, with the 3-trimethoxysilylpropyl group present in compound V, the rate of attack of hydroxide on the free base A is appreciable. This phenomena undoubtedly arises from intramolecular interactions of the hydrolyzed trimethoxysilyl group with the imidazoline ring. Such interactions could lead to sufficient reduction of the electron density about the center of reaction to allow for direct attack by hydroxyl ion. This effect could be pictured in the transition state as coordination of the nitrogen of the imidazoline ring with the vacant 3d orbitals of the silicon in the hydrolyzed trimethoxysilyl group. The nitrogen atoms in such a system are pictured as being solvated through hydrogen bonding. Considerations of models show that a conformation such as that shown in VI is nearly strainless.



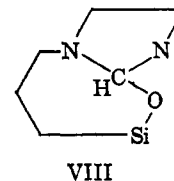
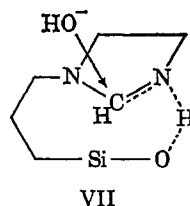
A sufficiently strong coordination with the silicon could lead to a system with an electron density at the center of reaction comparable with that of the transition state of the conjugate acid AH^+ . Coordination of nickel and copper ions with imino compounds has been demonstrated to dramatically enhance their rates of hydrolysis owing to similar reductions of electron den-

(9) G. L. Eichorn and I. M. Trachtenberg, *J. Am. Chem. Soc.*, **76**, 5183 (1954).

sity.⁹ Since the tendency of amino compounds to form complexes with silyl groups with less than three Si-O bonds is negligible,¹⁰ the effects seen here would be expected only in the case when R = (MeO)₃SiCH₂CH₂CH₂.

Other possible interactions could involve intramolecular hydrogen bonding with the imino nitrogen and a silanol as in VII or silicon-oxygen bond formation with the 2-carbon atom of the ring (VIII). In the latter case the intermediate B would result after hydrolysis of the silicon-oxygen-carbon bond. These intermediates resemble those advanced to explain the enhanced rates of hydrolysis for certain α -keto phosphates¹¹ and *p*-nitrophenyl salicylates.¹² However, with such interactions all of the methoxysilanes studied should show effects similar to V unless an unusual acidity for the corresponding silanol of V is postulated to explain its unique behavior.

(10) See, for example, C. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961).



(11) F. Ramirez, B. Hansen, and N. B. Desai, *ibid.*, **84**, 4588 (1962).
(12) M. L. Bender, F. J. Kezdy, and B. Zerner, *ibid.*, **85**, 3017 (1963).

Bistetracyclones and Bishexaphenylbenzenes. II

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Six additional representatives of the class of colored compounds, the bistetraphenylcyclopentadienones (1), have been prepared linked by (CH₂)₂, (CH₂)₃, (CH₂)₄, (CH₂)₅, and (CH₂)₆, respectively, and one in which one of the phenyl groups links two cyclopentadienone rings. New intermediates for their syntheses have been described including the required bisdeoxybenzoins and bisbenzils. Analogs of hexaphenylbenzene, melting in the range 337–470°, were prepared from each bistetraphenylcyclopentadienone by reaction with tolan. The absorption spectra of bistetracyclones and bishexaphenylbenzenes have been discussed based on tetracyclone and hexaphenylbenzene as models.

A previous paper³ discussed the syntheses and absorption spectra of the first four representatives of this new class of colored compounds, the bistetraphenylcyclopentadienones (1), in which the two tetraphenylcyclopentadienone moieties are linked directly by CH₂, O, and S, respectively. In the present paper we wish to report on the syntheses and absorption spectra of six additional bistetracyclones (1) and their corresponding bishexaphenylbenzenes (4).

Syntheses.—As outlined in our previous paper³ the route chosen to prepare the bistetraphenylcyclopentadienones consisted of the condensation of 2 moles of benzyl ketone with an appropriate bisbenzil. Charts I and II outline the paths selected.

Bibenzyl reacted with 2 moles of phenylacetyl chloride as described in the literature⁴ to give the bisdeoxybenzoin (2e). 1,3-Diphenylpropane, 1,4-diphenylbutane, 1,5-diphenylpentane, and 1,6-diphenylhexane also reacted with 2 moles of phenylacetyl chloride to give the bisdeoxybenzoins (2f–i) without exceptional difficulty. However, the bisphenylacetyl derivative of benzene could not be prepared this way; instead, it was prepared by the addition of a large excess of benzylmagnesium chloride (8 moles/nitrile group) to terephthalonitrile, followed by acid hydrolysis, which gave the bisdeoxybenzoin (2j) in 28% yield.

Conversion of compounds 2e–j to the bisbenzils 3e–j was effected *via* condensation with *p*-nitrosodiethylamine followed by acid hydrolysis in 25–63% yield.

Potassium hydroxide catalyzed condensation of compounds 3e–i with benzyl ketone proceeded without particular difficulty to give the bistetracyclones, 1e–i. However, compound 3j did not condense with benzyl ketone under these conditions, but was converted to the bistetracyclone 1j using *n*-butyl alcohol as solvent and Triton B (benzyltrimethylammonium hydroxide) as the base in 46% yield.

For derivative purposes the bistetracyclones were converted to the hexaphenylbenzene analogs by reaction with diphenylacetylene. As with the previously reported bistetracyclones, the melting points of the diphenylacetylene derivatives of this series of bistetracyclones are unusually high. The observed melting points range from 4h, m.p. 337–340° dec., to 4j, m.p. 468–470° (lit.⁵ m.p. 462–463° uncor.).

To complete the family of bishexaphenylbenzene analogs prepared, the missing member, 2',3',5',6',-2'',3'',5'',6''-octaphenylquaterphenyl (4k) was prepared by treating 2 moles of tetracyclone with 1 mole of diphenyldiacetylene. Chart III outlines the path.

The diphenyldiacetylene required was prepared by the Fieser modification⁶ of the Glaser reaction of phenylacetylene as reported in the literature.⁷

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