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Polymeric Schiff Bases. III. Some Prototype Exchange Reactions of Schiff Bases

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Summary

The amine moiety in Schiff bases can be exchanged quantitatively by another amine to yield new Schiff bases if the volatility of the replacing amine is lower than the derived amine, thereby allowing the latter to distilled from the reaction mass. This amine exchange was shown to be quantitative also for diamines and di-Schiff bases. Similarly, quantitative conversions were found for aldehydes and acetal exchanges with Schiff bases for both monofunctional and difunctional reactants. The bis exchange, involving two complementary Schiff bases, was quantitative also when the reactants were so selected that one of the new derived Schiff bases could be removed by distillation. The bis exchange was demonstrated with mono- and di-Schiff bases.

Mechanisms are suggested for these Schiff base exchange reactions: attempts to isolate the proposed intermediates physically were unsuccessful; however spectroscopic evidence indicates the formation of intermediate compounds.

The Schiff base exchanges involving polyfunctional reactants are of interest in the synthesis of polymers.

The condensation of aromatic dialdehydes and aromatic diamines in suitable solvents yields low molecular weight Schiff base polymers in the form of insoluble, infusible brick dusts (*1–4*). The low molecular weights of these polymers have been attributed to the insolubility of the growing polymer chains in each other and in the

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reaction medium (5). This led us to investigate other derivatives of the aldehydes and amines as reactants for the synthesis of polymeric Schiff bases. Among these derivatives were the monomeric Schiff bases (1) of arylene dialdehydes, $\mathrm{ArN{=}HCAr'CH{=}NAr}$, for reaction with arylene diamines, $\mathrm{Ar'(NH_2)_2}$, and (2) of arylene diamines, $\mathrm{ArCH{=}NAr'N{=}HCAr}$, for reaction with dialdehydes, $\mathrm{Ar'(CHO)_2}$. Both of these reactions would involve an exchange of end groups in the di-Schiff base; in the first case it would involve an amine exchange [Eq. (1)] eliminating an aryl amine, $\mathrm{ArNH_2}$, and, in the second case it would be an aldehyde exchange [Eq. (2)] eliminating an aryl aldehyde, ArCHO:

$$n\mathrm{ArN{=}HCAr'CH{=}NAr'} + n\mathrm{H_2NAr'NH_2} \rightarrow 2n\mathrm{ArNH_2} + \left[\mathrm{{=}HCAr'CH{=}NAr'N{=}}\right]_n \tag{1}$$

$$n\mathrm{ArCH{=}NAr'N{=}HCAr} + n\mathrm{OHCAr'CHO} \rightarrow 2n\mathrm{ArCHO} + \left[\mathrm{{=}NAr'N{=}HCAr'CH{=}}\right]_n \tag{2}$$

The reaction of the two complementary di-Schiff bases was also contemplated (*1*) for polymer synthesis; this reaction would involve a bis exchange [Eq. (3)] between the end groups of the two di-Schiff bases with the elimination of a monomeric Schiff base, $\mathrm{ArCH{=}NAr}$, as the by-product:

$$n\mathrm{ArN{=}HCAr'CH{=}NAr} + n\mathrm{ArCH{=}NAr'N{=}HCAr} \rightarrow 2n\mathrm{ArCH{=}NAr} + \left[\mathrm{{=}HCAr'CH{=}NAr'N{=}}\right]_n \tag{3}$$

These exchange reactions apparently have not been applied previously to the synthesis of polymers. Before applying them to the preparation of polymers it was deemed advisable to confirm that these exchange reactions would be substantially free of side reactions, which would lead to undesirable by-products, and that the yields would be very high, if not quantitative. Further, to ascertain the suitability of the amine, the aldehyde, and the bis exchange reactions to polymerization systems, it was considered necessary to evaluate these exchanges in monomeric Schiff base systems, as prototypes for the polymer reactions. The literature on these types of exchange reactions is very meager and the broad aspects of the Schiff base exchange reactions, as such, have not been described.

AMINE EXCHANGE

In 1921 Reddelien and Danilof (6) described an exchange involving α-naphthylamine and diphenylketanil. When the naphthylamine and the ketanil were melted together, partial replacement of aniline occurred, giving rise to an equilibrium mixture of products:

$$(C_6H_5)_2C{=}NC_6H_5 + C_{10}H_7NH_2 \rightleftharpoons \underset{\text{(I)}}{(C_6H_5)_2C{=}NC_{10}H_7} + C_6H_5NH_2 \qquad (4)$$

Further, they found that when the aniline was distilled from the reaction mixture, the equilibrium was shifted favorably and a quantitative yield of the new ketanil (I) was obtained. They enumerated three factors which were considered as important to the reaction: (a) the volatility of the added amine, (b) the chemical affinity of the amine for the ketone moiety in the ketanil, and (c) the concentration of the amine. A reinvestigation of this amine exchange reaction was undertaken to determine the scope of the reaction for its possible application in polymerization reactions. Of the three conditions listed above, the first was found to be most important for our purposes. When the volatility of the replacing amine is low in comparison to the derived amine, very high yields of final product can be obtained simply by selectively distilling out the derived amine.

Our studies showed that the amine exchange was not limited to ketanils but was used successfully with aldehyde-derived Schiff bases, ArCH=NAr. Further, the amine exchange was found to be applicable to polyfunctional amines and to polyfunctional Schiff bases. In the cases studied in Table 1, a quantitative yield of crude product was obtained. The melting points were determined on recrystallized samples. The melting point of 50 wt. % mixtures with authentic samples previously prepared and reported (8) showed no depression of the melting temperatures.

The results in our investigation of the amine exchange reaction appear to substantiate the original mechanism proposed (6) by Reddelien, which involves the reversible formation of an intermediate by the addition of the amine to the carbon-nitrogen double bond of the Schiff base. The literature (7) gives some basis for this first step. When acetaldehyde reacts with 2 moles of aniline, a diamine is obtained as the result of the formation initially of a Schiff base followed by the addition of a second mole of aniline to the base:

$$CH_3CHO + C_6H_5NH_2 \rightarrow CH_3CH{=}NC_6H_5 \xrightarrow{C_6H_5NH_2} CH_3CH(NHC_6H_5)_2 \qquad (5)$$

Under the reaction conditions, the intermediate decomposes to

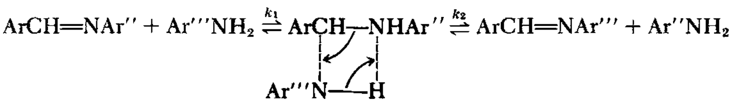
TABLE 1

Synthesis of Some Schiff Bases by Amine Exchange

Reagents			
A	B	Product	M.p. (8), °C[a]
$C_6H_5CH{=}NC_6H_5$	p-$ClC_6H_4NH_2$	$C_6H_5CH{=}NC_6H_4Cl$	62
$C_6H_5CH{=}NC_6H_5$	p-$O_2NC_6H_4NH_2$	$C_6H_5CH{=}NC_6H_4NO_2$	93
$C_6H_5CH{=}NC_6H_5$	p-$NH_2C_6H_4OCH_3$	$C_6H_5CH{=}NC_6H_4OCH_3$	72
p-$ClC_6H_4CH{=}NC_6H_5$	p-$NH_2C_6H_4Cl$	$ClC_6H_4CH{=}NC_6H_4Cl$	112
$2C_6H_5CH{=}NC_6H_5$	p-$NH_2C_6H_4NH_2$	$C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$	140
$2p$-$ClC_6H_4CH{=}NC_6H_5$	p-$NH_2C_6H_4NH_2$	$ClC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4Cl$	199
$2p$-$FC_6H_4CH{=}NC_6H_5$	p-$NH_2C_6H_4NH_2$	$FC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4F$	175
$2C_6H_5CH{=}NC_6H_5$	p-$NH_2C_6H_4CH_2C_6H_4NH_2$-p	$C_6H_5CH{=}NC_6H_4CH_2C_6H_4N{=}HCC_6H_5$	130
$2C_6H_5CH{=}NC_6H_5$	p-$NH_2C_6H_4OC_6H_4NH_2$-p	$C_6H_5CH{=}NC_6H_4OC_6H_4N{=}HCC_6H_5$	183
p-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-$p$	$2m$-$CH_3OC_6H_4NH_2$	$CH_3OC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4OCH_3$	221
p-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-$p$	$2p$-$ClC_6H_4NH_2$	$ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl$	180

[a] All melting points were taken on a calibrated Fisher-Johns melting point apparatus.

give an equilibrium concentration of the exchange products



$$\mathrm{ArCH{=}NAr'' + Ar'''NH_2 \overset{k_1}{\rightleftharpoons} \underset{Ar'''N{-}H}{ArCH{-}NHAr''} \overset{k_2}{\rightleftharpoons} ArCH{=}NAr''' + Ar''NH_2} \qquad (6)$$

If reactants are selected so that $Ar''NH_2$ is the most volatile of all the products in the mixture, then removal by distillation drives the reaction to completion.

In attempts to demonstrate the existence of an intermediate, an equimolar mixture of N,N-dimethyl-*p*-phenylenediamine and benzylidene aniline were heated together as a melt in a nitrogen atmosphere at 120°C, and samples withdrawn at 5-min intervals, dissolved in chloroform, their infrared spectra recorded, and the transmittance ratios of the NH_2 at 3380 cm^{-1} to —C—N— at 1250 cm^{-1}, and of C═N (1625 cm^{-1}) to —C—N— at 1250 cm^{-1} bonds evaluated. The data are shown in Table 2.

TABLE 2

Infrared Spectral Data of an Amine Schiff Base Exchange Reaction

Reaction time, min	Presence of NH_2	Transmittance ratio[a] NH_2/—C—N—	Presence of C═N	Transmittance ratio[a] C═N/—C—N—
0	Yes	—	Yes	—
5	Yes	0.338	Yes	1.235
10	Yes	0.284	Yes	0.746
15	Yes	0.200	Yes	0.690
20	Yes	0.260	Yes	—

[a] Measured on a Perkin-Elmer Model 421 infrared spectrometer.

The results indicate that as the reaction proceeds, the NH_2 and C═N bond absorptions decrease most probably through the formation of a complex, and that toward the end of the reaction the absorptions due to these two bonds increase again as exchange occurs and the chromophores reappear.

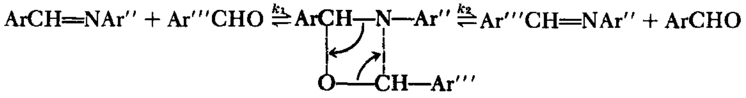
ALDEHYDE EXCHANGE

The aldehyde exchange is a reaction that is complementary to the amine exchange. In 1925 Ingold (9) reacted a few Schiff bases and aldehydes in suitable solvents at room temperature and in a few days was able to achieve equilibrium mixtures,

$$\mathrm{ArCH{=}NR'' + Ar'''CHO \rightleftharpoons Ar'''CH{=}NAr'' + ArCHO} \tag{7}$$

On reinvestigating this reaction, it was found that when it was performed in the absence of a solvent and the derived aldehyde removed by distillation, quantitative yields of the new Schiff base could be obtained. The reaction proceeds in the absence of catalysts, but it is accelerated, as is the amine exchange, by catalytic quantities of Lewis acids. Zinc chloride was found to be a particularly effective catalyst. The aldehyde exchange was found to be as facile as the amine exchange even when a variety of reagents was used and the reagents were bifunctional. A number of Schiff bases synthesized by the aldehyde exchange method are given in Table 3; their melting points and infrared spectra were compared with compounds which have been previously reported (*8*).

A mechanism for the aldehyde exchange reaction was proposed by Ingold (*9*), involving the intermediary of a four-membered oxazetidine ring, which was similar to the mechanism proposed by Reddelien (*6*) for the amine exchange reaction:

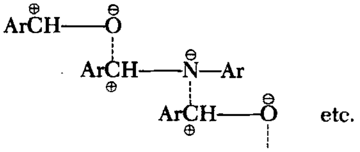


(8)

(II)

Although attempts by Ingold and by us to isolate physically the oxazetidine intermediate (II) were unsuccessful, the results obtained in this investigation appear to substantiate this mechanism. If the reactants are selected so that ArCHO is the most volatile of the products in the mixture, the removal of the formed ArCHO causes the reaction to be completed.

An alternative mechanism, which can be proposed for the aldehyde exchange, is that of the concerted type, wherein the intermediate can be written



in which the dipoles of the polarized aldehyde and Schiff base are aligned in such a manner that exchange can occur by a simple shift of electrons.

TABLE 3

Synthesis of Some Schiff Bases by Aldehyde Exchange

Reagents		Product	M.P. (8), °C[a]
A	B		
$C_6H_5CH{=}NC_6H_5$	*m*-$NO_2C_6H_4CHO$	*m*-$O_2NC_6H_4CH{=}NC_6H_5$	66
$C_6H_5CH{=}NC_6H_5$	*p*-HOC_6H_4CHO	*p*-$HOC_6H_4CH{=}NC_6H_5$	200
$C_6H_5CH{=}NC_6H_5$	*p*-ClC_6H_4CHO	*p*-$ClC_6H_4CH{=}NC_6H_5$	61
$C_6H_5CH{=}NC_6H_5$	*p*-BrC_6H_4CHO	*p*-$BrC_6H_4CH{=}NC_6H_5$	73
$2C_6H_5CH{=}NC_6H_5$	*p*-$OHCC_6H_4CHO$	*p*-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$	166
2*p*-$C_6H_5CH{=}NC_6H_4Cl$	*p*-$OHCC_6H_4CHO$	*p*-$ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl$-*p*	180
2*p*-$C_6H_5CH{=}NC_6H_4OCH_3$	*p*-$OHCC_6H_4CHO$	*p*-$CH_3OC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4OCH_3$-*p*	221
m-$C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$-*m*	2*p*-$O_2NC_6H_4CHO$	*p*-$O_2NC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4NO_2$-*p*	249
p-$C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$-*p*	2*m*-$O_2NC_6H_4CHO$	*m*-$O_2NC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4NO_2$-*m*	251
p-$C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$-*p*	2*p*-ClC_6H_4CHO	*p*-$ClC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4Cl$-*p*	199

[a] All melting points were taken on a calibrated Fisher-Johns melting point apparatus.

TABLE 4

Infrared Data of Aldehyde Schiff Base Exchange Reaction

Reaction time, min	Presence of —CHO	Transmittance ratio[a] ArCH/HC═O	Presence of C═N	Transmittance ratio[a] CH═N/ArCH
0	Yes	0.754	Yes	1.033
5	Yes	0.754	Yes	1.150
7	Yes	0.740	Yes	1.000
10	Yes	0.756	Yes	0.855
15	Yes	0.794	Yes	0.956

[a] Measured on a Perkin-Elmer Model 421 infrared spectrometer.

In attempts to confirm the presence of an intermediate, an equimolar mixture of *p*-nitrobenzaldehyde and benzylideneaniline were heated together at 110°C, samples withdrawn at 5-min intervals, dissolved in chloroform, their infrared spectra recorded, and the transmittance ratios of characteristic bonds for

$$\mathrm{Ar}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}$$

at 2700 cm^{-1}, HC═O at 1700 cm^{-1}, and C═N at 1625 cm^{-1} evaluated as in the case of the amine exchange. The data are shown in Table 4.

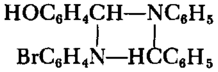
As was observed in the amine exchange reaction, the C═O and the C═N bond absorptions decreased to a minimum during the course of the reaction and thereafter increased as the exchange occurs. This evidence serves to lend some weight to the existence of a four-membered ring intermediate, particularly in view of the fact that no noticeable increase in viscosity of the mixture during the reaction was observed; such an increase should be expected if a concerted mechanism was operative which would result in an intermediate ionic-type polymer.

BIS EXCHANGE

Exchange can also take place between two different Schiff bases. Ingold and Piggot (*10*) in 1922 reported that if two simple Schiff bases are mixed together in solution, an equilibrium mixture of reactants and products arising by the exchange between the two Schiff bases [Eq. (9)] is obtained:

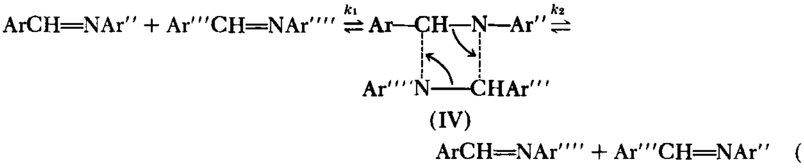
$$p\text{-}\mathrm{HOC_6H_4CH{=}NC_6H_5} + p\text{-}\mathrm{BrC_6H_4N{=}CHC_6H_5} \rightleftharpoons p\text{-}\mathrm{HOC_6H_4CH{=}NC_6H_4Br} + \underset{\text{(III)}}{\mathrm{C_6H_5CH{=}NC_6H_5}} \quad (9)$$

Also reported (*10*) was the isolation of the diazetidine intermediate,



$$\begin{array}{l}\mathrm{HOC_6H_4CH{-}NC_6H_5}\\ \quad\;\;|\qquad\;|\\ \mathrm{BrC_6H_4N{-}HCC_6H_5}\end{array}$$

which underwent decomposition to the two new Schiff bases. This reaction, which we have termed the "bis exchange reaction," was investigated. Our attempts to isolate the diazetidine intermediate were, after many attempts, inconclusive, but, by applying the techniques used in the preceding exchange reactions, melting the reactants together in the absence of a solvent and distilling out one of the most volatile (III) Schiff base, it was possible to drive the reaction to completion. As in the amine and aldehyde exchanges, the reactants must be selected so that one of the product Schiff bases is more volatile than the reactants. The results of a number of bis exchange reactions given in Table 5 appear to substantiate the mechanism proposed by Ingold and Piggot (*10*),

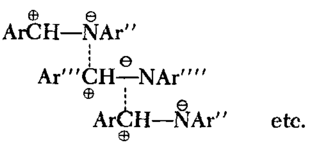


(IV)

(10)

$$\mathrm{ArCH{=}NAr'' + Ar'''CH{=}NAr''''} \overset{k_1}{\rightleftharpoons} \underset{\text{(IV)}}{\begin{array}{c}\mathrm{Ar{-}CH{-}N{-}Ar''}\\ \vdots\qquad\vdots\\ \mathrm{Ar'''N{-}CHAr'''}\end{array}} \overset{k_2}{\rightleftharpoons} \mathrm{ArCH{=}NAr'''' + Ar'''CH{=}NAr''} \quad (10)$$

A concerted mechanism of the type



$$\begin{array}{l}\mathrm{Ar\overset{\oplus}{C}H{-}\overset{\ominus}{N}Ar''}\\ \qquad\quad\vdots\\ \quad\mathrm{Ar'''\underset{\oplus}{C}H{-}\overset{\ominus}{N}Ar''''}\\ \qquad\qquad\vdots\\ \qquad\mathrm{Ar\underset{\oplus}{C}H{-}\overset{\ominus}{N}Ar''} \qquad \text{etc.}\end{array}$$

can also be proposed for the bis-Schiff base exchange reaction in which the exchange can occur in a chain-type reaction by a shift of electrons.

In attempts to confirm the existence of an intermediate such as (IV), a number of the pairs of reagents of Table 5 were reacted at 100°C and the infrared and ultraviolet spectra of the reaction mixtures recorded and evaluated. Because of overlap of spectral regions, the interpretations of these data yielded no convincing evi-

TABLE 5

Synthesis of Some Schiff Bases by Bis Exchange Reactions

Reagents			
A	B	Product	M.p. (8), °C[a]
$C_6H_5CH{=}NC_6H_4OCH_3$-*p*	$C_6H_5N{=}HCC_6H_4NO_2$-*p*	*p*-$O_2NC_6H_4CH{=}NC_6H_4OCH_3$-*p*	135
$C_6H_5CH{=}NC_6H_4Cl$-*p*	$C_6H_5N{=}HCC_6H_4Cl$-*p*	*p*-$ClC_6H_4CH{=}NC_6H_4Cl$-*p*	112
$C_6H_5CH{=}NC_6H_4Cl$-*p*	*p*-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-*p*	*p*-$ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl$-*p*	180
$C_6H_5CH{=}NC_6H_4OCH_3$-*p*	*p*-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-*p*	*p*-$CH_3OC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4OCH_3$-*p*	221
p-$ClC_6H_4CH{=}NC_6H_5$	*p*-$C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$-*p*	*p*-$ClC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4Cl$-*p*	199

[a] All melting points were taken on a calibrated Fisher-Johns melting point apparatus.

dence of the existence of a four-membered ring intermediate. However, the absence of any noticeable increase in viscosity of the mixture during reaction tends to eliminate the concerted mechanism.

ACETAL EXCHANGE

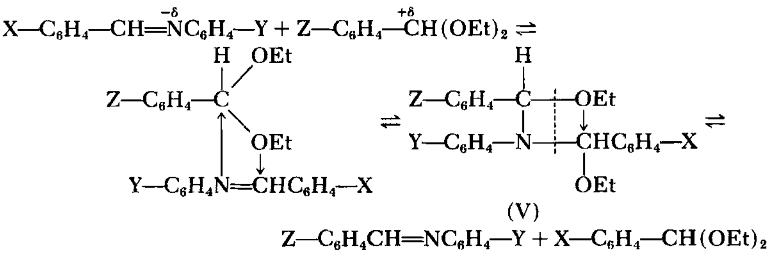
Another Schiff base exchange reaction, which appears to be unreported in the literature, was also studied. Aromatic acetals were observed to react with Schiff bases [Eq. (11)] in a fashion similar to the aldehyde exchange:

$$ArCH{=}NAr'' + Ar'''CH(OR)_2 \rightleftharpoons Ar'''CH{=}NAr'' + ArCH(OR)_2 \qquad (11)$$

This reaction was found to proceed readily in the presence of toluene sulfonic acid or other Lewis acids at temperatures in the range 150–170°C, whereas generally, in the absence of a catalyst, reaction failed to occur except in the case of the nitro-Schiff bases, $O_2NC_6H_4CH{=}NAr$. A number of Schiff bases prepared by reacting a monoacetal, $ArCH(OR)_2$, or a diacetal, $(RO)_2HCAr'CH(OR)_2$, with an appropriate Schiff base with toluene sulfonic acid as the catalyst are given in Table 6.

To confirm the need of a catalyst in these reactions and to obtain data on which to base a mechanism, a series of experiments was performed at temperatures varying from room temperature to 220°C, without and with catalysts, and, with —H, —Cl, and $—NO_2$ substituents in the reagents. The course of the reaction was followed by recording changes in the infrared spectra of the reaction mixtures. The data for the uncatalyzed reaction is shown in Table 7 and for the catalyzed reaction in Table 8.

On the basis of the infrared spectral data and that of Tables 6–8, the following mechanism, Eq. (12), is proposed for the actual Schiff base exchange reaction:



$$X{-}C_6H_4{-}CH{=}\overset{-\delta}{N}C_6H_4{-}Y + Z{-}C_6H_4{-}\overset{+\delta}{C}H(OEt)_2 \rightleftharpoons \begin{array}{c} H \quad OEt \\ Z{-}C_6H_4{-}C \\ \uparrow \qquad OEt \\ \downarrow \\ Y{-}C_6H_4N{=}CHC_6H_4{-}X \end{array} \rightleftharpoons \begin{array}{c} H \\ Z{-}C_6H_4{-}C{-}OEt \\ Y{-}C_6H_4{-}N{-}CHC_6H_4{-}X \\ OEt \\ (V) \end{array} \rightleftharpoons Z{-}C_6H_4CH{=}NC_6H_4{-}Y + X{-}C_6H_4{-}CH(OEt)_2 \qquad (12)$$

The principal absorption peaks at 1625 cm^{-1} for C=N and at 1055 cm^{-1} and 1100 cm^{-1} for the acetal,

TABLE 6

Synthesis of Some Schiff Bases by Catalyzed Acetal Exchange

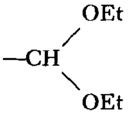
Reagents			
A	B	Product	M.p. (8), °C[a]
$C_6H_5CH{=}NC_6H_5$	p-$O_2NC_6H_4(OC_2H_5)_2$	p-$O_2NC_6H_4CH{=}NC_6H_5$	66
$C_6H_5CH{=}NC_6H_5$	p-$ClC_6H_4CH(OC_2H_5)_2$	p-$ClC_6H_4CH{=}NC_6H_5$	61
$C_6H_5CH{=}NC_6H_4Cl$-p	p-$ClC_6H_4CH(OC_2H_5)_2$	p-$ClC_6H_4CH{=}NC_6H_4Cl$-p	112
$2C_6H_5CH{=}NC_6H_5$	p-$(H_5C_2O)_2HCC_6H_4CH(OC_2H_5)_2$-$p$	p-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-$p$	166
$2C_6H_5CH{=}NC_6H_5$	p-$(H_9C_4O)_2HCC_6H_4CH(OC_4H_9)_2$-$(p)$	p-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-$p$	166
$2C_6H_5CH{=}NC_6H_4Cl$-p	p-$(H_5C_2O)_2HCC_6H_4CH(OC_2H_5)_2$-$(p)$	p-$ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl$-$p$	180
p-$ClC_6H_4CH{=}NC_6H_5$	p-$(H_5C_2O)_2HCC_6H_4CH(OC_2H_5)_2$-$(p)$	p-$C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$-$p$	166

[a] All melting points were taken on a calibrated Fisher-Johns melting point apparatus.

TABLE 7

Results of Uncatalyzed Reaction between p-$XC_6H_4CH{=}NC_6H_4Y$-p and p-$ZC_6H_4CH(OC_2H_5)_2$ Under Various Conditions

Substituents			Reaction temp., °C	Reaction time, hr	Infrared evidence of reaction
X	Y	Z			
H	H	H	25	72.0	Negative
H	H	H	40	2.0	Negative
H	H	H	130	18.0	Negative
H	H	H	160	6.0	Negative
H	H	H	180	16.0	Negative
Cl	H	H	88	4.0	Negative
Cl	H	H	150	28.0	Negative
Cl	H	H	220	35.0	Negative
NO_2	H	H	150	1.5	Negative
NO_2	H	H	150	7.0	Negative
NO_2	H	H	150	24.0	Negative
NO_2	H	H	150	30.0	Positive
H	H	Cl	120	45.0	Positive
H	H	Cl	180	2.0	Positive



$$-CH(OEt)_2$$

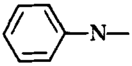
decrease substantially, except for the peak at 1100 cm^{-1}, as the reaction proceeds. The 1100 cm^{-1} band is characteristic of an ether

TABLE 8

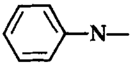
Results of Catalyzed Reaction between p-$XC_6H_4CH{=}NC_6H_4Y$-p and p-$ZC_6H_4CH(OC_2H_5)_2$ Under Various Conditions

Substituents			Reaction temp., °C	Reaction time, hr	Infrared evidence of reaction
X	Y	Z			
H	H	H	140	0.25	Negative
H	H	H	140	7.00	Positive
Cl	H	H	140	0.25	Negative
Cl	H	H	140	7.00	Positive
NO_2	H	H	140	0.25	Negative
NO_2	H	H	140	7.00	Positive

linkage. Further, the absorptions at 1600 cm^{-1} attributed to ring stretching in

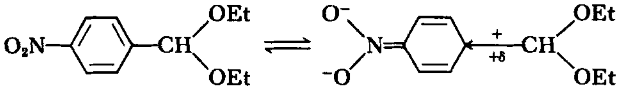


and at 1330 cm^{-1} attributed to —C—N stretching in

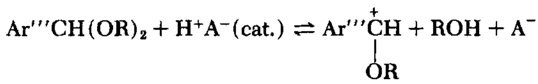


increased with reaction time, indicating the formation of the intermediate compound.

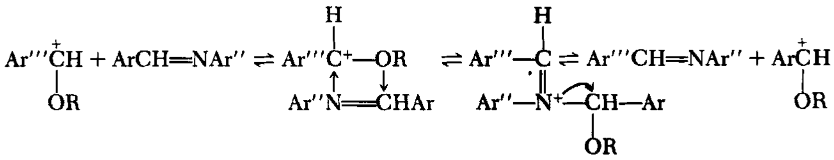
These decays in the infrared spectra offered good evidence for the proposed mechanism and were found in the uncatalyzed reactions in which reaction occurred as well as in all the catalyzed reactions. In the reaction mechanism proposed above, if the substituent X is highly electron-withdrawing, the positive character of the attacking carbon atom of the acetal is enhanced,



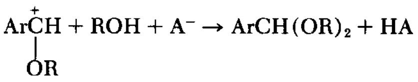
thereby facilitating the nucleophilic attack of the negative nitrogen atom of the Schiff base to form the intermediate (V). In this case, a catalyst was not required to obtain the reaction. In those reactions in which the nitro group was present as a substituent, there was also evidence of side reactions which led to discoloration of the reaction mixture and to reduced yields, which in some cases were less than 50% of the calculated value, and to the formation of by-products. Without a highly electron-withdrawing substituent on the aromatic ring of the acetal, a catalyst was found to be needed to promote the reaction. Then the electropositive species formed by the protonation of the catalyst attacks the unpaired electrons of the nitrogen atom of the Schiff base, thereby becoming the intermediate; thus



$$\mathrm{Ar'''CH(OR)_2 + H^+A^-(cat.) \rightleftharpoons Ar'''\underset{OR}{\overset{+}{C}}H + ROH + A^-}$$



$$\mathrm{Ar'''\underset{OR}{\overset{+}{C}}H + ArCH{=}NAr'' \rightleftharpoons \begin{array}{c} H \\ Ar'''C^+{-}OR \\ \uparrow \quad \downarrow \\ Ar''N{=}CHAr \end{array} \rightleftharpoons \begin{array}{c} H \\ Ar'''{-}C \\ \| \\ Ar''{-}N^+{-}CH{-}Ar \\ OR \end{array} \rightleftharpoons Ar'''CH{=}NAr'' + Ar\underset{OR}{\overset{+}{C}}H}$$



$$\mathrm{Ar}\underset{\mathrm{OR}}{\overset{+}{\mathrm{C}}}\mathrm{H} + \mathrm{ROH} + \mathrm{A}^- \rightarrow \mathrm{ArCH(OR)_2} + \mathrm{HA} \qquad (13)$$

The acetal exchange reaction with Schiff base [Eq. (13)] differs from the acetals with the free amine [Eq. (14)]. This latter reaction,

$$\mathrm{ArCH(OR)_2} + \mathrm{ArNH_2} \rightarrow \mathrm{ArCH{=}NAr} + 2\mathrm{ROH} \qquad (14)$$

does not appear to be described in the literature and proceeds in the absence of catalysts, although it is accelerated greatly by Lewis acids. For comparison with the acetal Schiff base exchange reactions reported here, this acetal-amine reaction was studied also and is the subject of another communication.

The syntheses of Schiff base polymers by means of Schiff base exchange reactions is the subject of a separate communication.

EXPERIMENTAL

The synthesis and purification of the reactants used in these syntheses, with the exception of the acetals, were reported (*8*) previously.

Synthesis of Acetals

Benzylidenediethyl ether, $C_6H_5CH(OC_2H_5)_2$, was prepared from 1.0 mole of benzaldehyde and 1.1 mole of ethyl orthoformate with 2 wt. % of the reactants of *p*-toluenesulfonic acid using the procedure reported (*11*) by Post; b.p. 223°C/760 mm Hg; 108°C/20 mm Hg; 93°C/10 mm Hg; lit. (*11*) b.p. 222°C/760 mm Hg; yield 75%.

p-Chlorobenzylidenediethyl ether, *p*-$ClC_6H_4CH(OC_2H_5)_2$, was prepared from *p*-chlorobenzaldehyde and ethyl orthoformate by the same procedure used for benzylidenediethyl ether; b.p. 129–130°C/15 mm; yield 83%.

Analysis: Calcd.: C, 61.54%; H, 6.99%; Cl, 16.54%
Found: C, 61.97%; H, 7.04%; Cl, 16.66%

p-Nitrobenzylidenediethyl ether, *p*-$O_2NC_6H_4CH(OC_2H_5)$, was prepared from *p*-nitrobenzaldehyde and ethyl orthoformate by the same procedure used above; b.p. 137–138°C/3 mm Hg; yield 86%.

Analysis: Calcd.: C, 58.66%; H, 6.66%; N, 6.22%
Found: C, 58.73%; H, 6.61%; N, 6.24%

p-Xylylidenetetraethyl ether, $(H_5C_2O)_2HCC_6H_4CH(OC_2H_5)_2$, was prepared by 116 g of terephthaldehyde, 330 g of ethyl orthoformate, and 3 of *p*-toluenesulfonic acid by the same procedure given above and collecting 150 g of ethyl formate on distillation of the reaction mixture. Then solid anhydrous sodium carbonate was added to the cooled reaction mixture which was allowed to stand for 8 hr, then filtered to remove solid matter, and distilled. B.p. 147–148°C/3.2 mm Hg, 144–145°C/3 mm Hg, $n_D^{20} = 1.4742$; yield 75%. The purity as determined by gas chromatography in an F and M Model 609 flame ionization chromatograph with a 10-ft column of Carbowax 1500 at 150°C was greater than 99.9%.

Analysis: Calcd.: C, 68.05%; H, 9.31%
Found: C, 68.02%; H, 9.30%

p-Xylylidenetetra-*n*-butyl ether, $(H_9C_4O)_2HCC_6H_4CH(OC_4H_9)_2$. A mixture of 134 g (1.0 mole) of terephthaldehyde, 333 g of *n*-butyl alcohol (4.5 moles), 4 g of *p*-toluenesulfonic acid, and 800 ml of toluene were placed in a 1-liter single-neck ground-glass flask fitted with a Dean-Stark apparatus, reflux condenser, and electric heating mantle. The mixture was refluxed for 11 hr and 17.8 g of water (99% of theory). After cooling to room temperature, the mixture was neutralized with 10% aqueous sodium carbonate, dried over anhydrous sodium carbonate, and fractionally distilled; yield 87%. B.p. 163°C/0.4 mm Hg. The purity, as determined by gas chromatography, was greater than 99.9%.

Analysis: Calcd.: C, 72.13%; H, 10.38%
Found: C, 72.10%; H, 10.37%

Exchange Reactions

Since the procedure used was substantially the same for all the exchange reactions, it will be described in general terms and illustrated by a few specific examples. All reactions were performed under a deoxygenated nitrogen atmosphere to avoid possible oxidation of any of the products at the temperatures used. The reactions were performed by placing equivalent quantities of the reactants in a round-bottom, ground-glass jointed flask equipped with a nitrogen gas inlet, a distilling head, condenser, and a receiver equipped for attachment to a reduced pressure source. The reaction vessel was equipped with an electric heating mantle controlled by a variable transformer. The nitrogen flow was then started and the mixture heated to 10–20°C above its melting point and held there until a clear melt was obtained; then the temperature was raised slowly to the temperature at which the by-product distills at atmospheric or at a selected reduced pressure. The reaction was continued until the calculated amount of by-product was collected. The contents of the flask were then allowed to cool to room temperature, weighed, and then recrystallized (*8*) from 95% ethanol, or benzene, or a mixture of both.

Dibenzylidene-*p*-phenylenediamine. *p*-Phenylenediamine, 1.350 g (0.0125 mole), 4.53 g (0.025 mole) of benzylideneaniline, and 10 mg of $ZnCl_2$ were mixed in a 50-ml round-bottom microflask equipped with a nitrogen inlet, distilling head, receiver, etc. Under a slow stream of nitrogen, the mixture was heated to 110°C, at which temperature a clear melt was obtained and reflux began. Then after 15 min the temperature was raised slowly to 150°C, held there for 10 min, and the reaction terminated. The yields of aniline collected and of the crude product were quantitative. Recrystallization of product from 95% ethanol gave a product which melted at 140°C and which was not depressed by mixture with an authentic sample (*8*). Its infrared spectrum was also identical to that of the authentic sample.

p-Xylylidene-*p*-methoxyaniline. A mixture of 2.46 g (0.02 mole) of *p*-anisidine and 2.84 g (0.01 mole) of terephthaldianil without catalyst were reacted in the apparatus by the procedure described except that, in the absence of a catalyst, the reaction was slower and a temperature of 200°C was used, and the reaction continued for 2 hr. The yield of crude product was quantitative and its m.p. was 219°C. The melting point, 221°C, of the recrystallized product and its infrared spectrum were identical to those of an authentic sample (*8*).

p-Xylylidenedianiline. A mixture of 4.53 g (0.025 mole) of benzylidene aniline, 1.7 g (0.0123 mole) of terephthaldehyde, and 10 mg of $ZnCl_2$ were reacted in the microapparatus, described above, at a maximum temperature of 200°C. The calculated amount of aniline was collected in 90 min and the yield of crude product was quantitative. The melting point, 166°C of the product recrystallized from ethanol and its infrared spectrum were identical to those of an authentic sample (*8*).

di-m-Nitrobenzylidene-*p*-phenylenediamine. A mixture of 3.02 g

(0.02 mole) of *m*-nitrobenzaldehyde and 2.84 g (0.01 mole) of dibenzylidene-*p*-phenylenediamine without catalyst were reacted in the microapparatus at 130°C at 50–60 mm Hg pressure. The reaction was completed in 5 hr and a quantitative yield of crude product obtained. Recrystallization from ethanol or acetone yielded a product, m.p. 245°C, which corresponds to that of an authentic sample (*8*).

p-Nitrobenzylidene-*p*-methoxyaniline. A mixture of 2.26 g (0.01 mole) of *p*-nitrobenzylideneaniline, 2.11 g (0.01 mole) of benzylidene-*p*-anisidine, and 5 mg of $ZnCl_2$ were reacted in the microapparatus at 200°C for 1 hr at atmospheric pressure, then at 5 mm Hg pressure for 12 hr, and benzylideneaniline collected as the distillate. The yield of crude product was quantitative. Recrystallization from ethanol yielded a product, m.p. 139°C, which was not changed when mixed with an authentic sample (*8*).

p-Chlorobenzylideneaniline. A mixture of 1.81 g (0.01 mole) of benzylideneaniline and 2.13 g (0.01 mole) of *p*-chlorobenzylidenediethyl ether and 0.05 g of *p*-toluenesulfonic acid were reacted in the microapparatus at 170°C for 30 min at 760 mm, 60 min at 40 mm Hg, and 10 min at 10 mm Hg pressure and the reaction terminated. The distillate consisted of $C_6H_5CH(OC_2H_5)_2$ and the yield of crude product was quantitative. Recrystallization from ethanol or hexane gave a product whose m.p., 62°C, and infrared spectrum corresponded to that of an authentic sample (*8*).

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Zusammenfassung

Die Aminkomponente in Schiff'schen Basen kann quantititiv durch andere Amine ausgetauscht werden, wenn die Flüchtigkeit des ersetzenden Amines geringer ist als die des ursprünglich vorhandenen, wodurch letzteres aus der Reaktionsmischung herausdestilliert werden kann. Hierbei ergeben sich neue Schiff'sche Basen. Dieser Aminaustausch ist auch im Falle von Diaminen und Di-Schiff'schen Basen quantitativ. Ebenso ergaben sich quantitative Umsetzungen beim Austausch von Aldehyden und Acetalen mit Schiff'schen Basen, woebi die Verbindungen mono-als auch difunktionell sein können. Der difunktionelle Austausch zwischen komplementären Schiff'schen Basen war auch dann quantitativ, wenn die reagierenden Verbindungen so ausgewählt waren, dass eine der neu entstandenen Schiff'schen Basen durch Destillation abgetrennt werden konnte. Dieser zweifache Austausch konnte mit Mono und Di-Schiff'schen Basen durchgeführt werden.

Für den Austausch von Schiff'schen Basen werden Mechanismen vorgeschlagen, woebi allerdings Versuche mit dem Ziel die angenommenen Zwischenprodukte zu isolieren, fehlschlugen. Spektroskopische Befunde sprechen jedoch für die Bildung von intermediären Verbindungen.

Der Austusch von polyfunktionellen Schiff'schen Basen ist für die Synthese von Polymeren von Interesse.

Résumé

La partie amine dans les bases de Schiff peut quantitativement être remplacée par une autre amine pour donner des bases de Schiff nouvelles, si la volatilité de l'amine échangeuse est plus basse que celle de l'amine remplacée, permettant ainsi la distillation de la derniére de la masse réactionelle. Cet échange d'amines est aussi quantitative dans le cas de diamines et de di-bases de Schiff. D'une maniére analogue on a trouvé des conversions quantitatives dans les échanges d'aldehydes et d'acétals avec les bases de Schiff pour des reactifs mono- et bifonctionnels. L'échange bis, avec deux bases de Schiff complémentaires, était quantitatif aussi dans le cas des réactifs selectionnés permettant l'élimination des bases de Schiff nouvelles, obtenues par distillation. Cet échange bis- a été demonstré avec des mono- et bi-bases de Schiff.

On suggère des mécanismes pour ces réactions d'échange de bases de Schiff; on n'a pas réussie a isoler les intermediaires proposés: cependant les donnéés spectroscopiques indiquent la formation de produits intermédiaires.

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