

(26%) and **5e** (46%) were isolated by chromatography in air of the reaction mixture of complex **2** with alkynes **3d** and **3e**. Although the mechanism of formation is not clear,<sup>13</sup> this reaction is a useful method of synthesis for a variety of unsymmetrically disubstituted 1,2-dithiolene-iron complexes containing a functional group.

The trigonal bipyramidal geometry of the dithiolene complexes **4** in solution is supported by <sup>1</sup>H and <sup>31</sup>P NMR which showed the trans position of identical phosphite ligands<sup>15</sup> and ruled out the square-pyramidal geometry.<sup>16</sup> A dimeric structure has also been ruled out.<sup>17</sup>

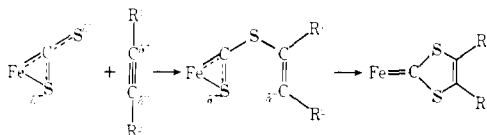
Finally it is worth noting that, after the air oxidation of the carbene complexes **4a** and **4c** besides the dithiolene derivatives **5a** and **5c**, we were able to isolate substituted tetrathiafulvalene derivatives resulting from duplication of 1,3-dithiolium carbenes. Thus the unsymmetrically (**7a**) or the symmetrically (**7c**) substituted tetrathiafulvalenes were obtained in 26 and 28% yields, respectively.<sup>18</sup>

The formation of carbene complexes from η<sup>2</sup>-CS<sub>2</sub>-iron complexes is not restricted to derivatives of the phosphite ligand P(OMe)<sub>3</sub>. We were also able to characterize similar 1,3-dithiolium-carbene complexes by addition of alkynes to Fe(η<sup>2</sup>-CS<sub>2</sub>)(CO)<sub>2</sub>L<sub>2</sub> derivatives when L is PMe<sub>3</sub> or PMe<sub>2</sub>Ph. We are currently investigating the influence of the phosphorus ligand on the competitive formation of dithiolene complexes and tetrathiafulvalenes.

**Acknowledgment.** The authors are grateful to Professor A. J. Carty and Dr. D. Touchard for stimulating discussions and to P. Guénot for mass spectral assistance. H. Le Bozec thanks the DGRST for financial support.

## References and Notes

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- (11) Spectroscopic data for **5a** are typical: mass spectrum (M<sup>+</sup>: found, 493.968; calcd, 493.968), (M - CO)<sup>+</sup> 466, (M - CO, -P(OMe)<sub>3</sub>)<sup>+</sup> 342; IR (Nujol) ν<sub>C=O</sub> 1965, ν<sub>C=S</sub> 1700 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.33 (H), 4.27 (q, CH<sub>2</sub>), 1.40 (t, CH<sub>3</sub>), 3.42 (t, OCH<sub>3</sub>) (<sup>3</sup>J<sub>P-H</sub> = 11.5 Hz).
- (12) **5a**: IR ν<sub>C=O</sub> 2030, 1985 cm<sup>-1</sup>; mass spectrum (M<sup>+</sup>: found, 397.935; calcd, 397.934), (M - CO)<sup>+</sup> 370, (M - 2CO)<sup>+</sup> 342.
- (13) Dithiolene complexes of the type M(CO)(PR<sub>3</sub>)<sub>2</sub>[S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>] have been formed by reacting the corresponding phosphorus ligand with [M(CO)<sub>3</sub>S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>x</sub> arising from the action of bis(trifluoromethyl)dithietene on metal carbonyls.<sup>14</sup> One possible route to complex **5** is via the dithietene formed by decomposition of the carbene ligand (or tetrathiafulvalene), although this was not observed in the present instance.
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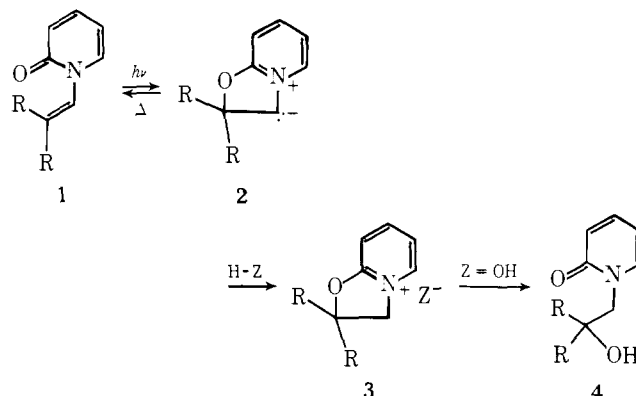
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Received January 9, 1978

## Kinetic Analysis and Solvent Polarity Effects on the Ylide-Forming Photocyclization Reaction of 1-Vinyl-2-pyridones<sup>1</sup>

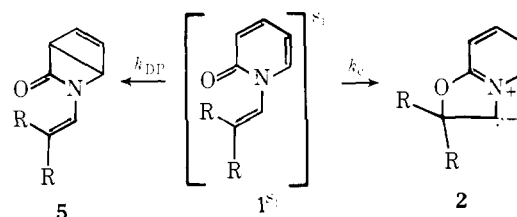
Sir:

Recently we uncovered a novel photochemical reaction in which 1-vinyl-2-pyridones (**1**) are converted to either oxazolo[3,2-a]pyridinium salts (**3**) or pyrid-2-on-ylethanols (**4**).<sup>1</sup>



Accumulated evidence suggested that (a) pyridinium azomethine ylides **2**, generated from singlet 1-vinyl-2-pyridones (**1**<sup>s1</sup>), are intermediates in this reaction, (b) alcohol products derive from initially formed pyridinium salts when hydroxide is the counterion (Z = OH<sup>-</sup>), and (c) ylides **2** rapidly revert to starting 1-vinyl-2-pyridones. The photochemical step in this process, involving electrocyclicization of the enamide grouping, mimics the analogous reactions followed by isoelectronic systems containing the divinylamine,<sup>2a</sup> ether,<sup>2a</sup> and sulfide<sup>2c</sup> chromophores.

The most significant of several preliminary observations derived from an investigation of the effect of water on the efficiencies of the familiar Dewar pyridone forming reaction (**1** → **5**)<sup>3</sup> (also a singlet process)<sup>4</sup> and competing photocyclization. The efficiency for production of **4** was found to increase at the expense of **5** as water concentration in H<sub>2</sub>O-THF solutions is increased, suggesting that partitioning of **1**<sup>s1</sup> to **5** and **2** (k<sub>DP</sub>/k<sub>c</sub>) is affected by solvent polarity or proton-donating ability. The synthetic and mechanistic importance of potential



**Table I.** Quantum Yields for Dewar Pyridone Formation from IBP

Solvent	$\tau$ , ns <sup>a</sup>	$\phi_{DP}$ <sup>b</sup>
CH <sub>3</sub> OH	7.3 ± 1.0	0.061
CH <sub>3</sub> CN	16.6	0.143
THF	30.0	0.260

<sup>a</sup> Degassed, nitrogen purged solutions were used at room temperature. <sup>b</sup> Reaction quantum yields were measured for product production using degassed, nitrogen-purged solutions and an optical bench apparatus. Light output was determined using potassium ferrioxalate actinometry.<sup>11</sup> Alcohol product analysis was performed by GLC using internal standards.

**Table II.** Quantum Yields for Oxazolopyridinium Salt Formation from IBP.

Water concn, M	HClO <sub>4</sub> concn, mM	Reaction quantum yields, <sup>b,c</sup> $\phi_f$
27.7 <sup>a</sup>	-0-	0.071
50.0 <sup>a</sup>	-0-	0.110
55.6	-0-	0.130
55.6	0.50	0.160
55.6	1.00	0.190
55.6	2.00	0.213
55.6	3.00	0.248
55.6	5.00	0.315

<sup>a</sup> Acetonitrile was used as cosolvent. <sup>b</sup> Footnote b in Table I. <sup>c</sup> The pyridinium salts obtained from irradiation of acid solutions were first converted to alcohol by treatment with base before analysis. Conversions to product were in the range of 11–17%. Estimated error for  $\phi_f$  measurements is 5%. Irradiations of aqueous solutions of the isobutenylpyridone in the absence of acid lead directly to the pyridonyl alcohol.

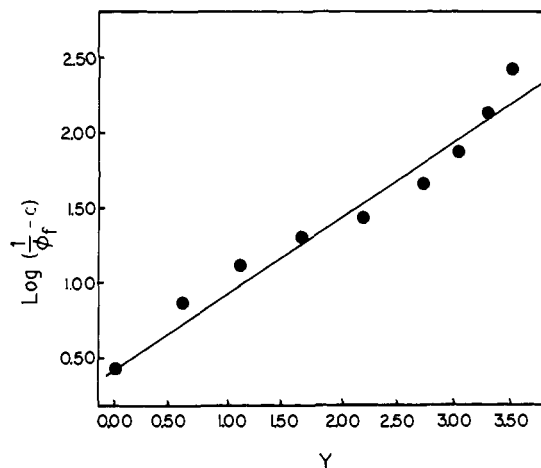
conclusions about solvent polarity effects on rates of singlet vinylpyridone to pyridinium ylide transformations prompted a detailed kinetic analysis of this process. This has led to several interesting conclusions.

Quantum yields for fluorescence ( $\phi_f$ ) and alcohol or salt formation ( $\phi_r$ ), and singlet lifetimes ( $\tau$ ) of the isobutenylpyridone (IBP) (**1**, R = CH<sub>3</sub>) in solvents of varying polarity and containing varying quantities of HClO<sub>4</sub> were measured. Inspection of the data reveals several interesting features. First,  $\phi_f$  (0.003 ± 0.001) and  $\tau$  (5.1 ± 1.0 ns) remain invariant with changes in [HClO<sub>4</sub>] in the range of 0.5 to 5.0 mM. Thus, solvent acidity has little effect on the rates of processes used by the singlet of IBP (IBP<sup>s1</sup>) for deactivation, ruling out pathways for the production of **3** or **4** involving protonation of **1**<sup>s1</sup>. Second, both  $\tau$  and  $\phi_f$  of IBP decrease dramatically as [H<sub>2</sub>O] in CH<sub>3</sub>CN solutions is increased. For example,  $\tau$  and  $\phi_f$  are 10.3 ± 1.0 ns and 0.007 ± 0.001, respectively, in 50% (v/v) H<sub>2</sub>O-CH<sub>3</sub>CN and 5.1 ± 1.0 ns and 0.003 ± 0.001 in water. Likewise,  $\phi_f$  was found to be similarly dependent upon the polarity of nonaqueous solvents. Importantly, changes in  $\phi_f$  and  $\tau$  are proportional so that  $k_f$  (6–7 × 10<sup>5</sup> s<sup>-1</sup>) is solvent polarity independent.<sup>5</sup> In addition,  $k_{DP}$  (8.6 × 10<sup>6</sup> s<sup>-1</sup>), calculated using the data in Table I, does not vary with solvent polarity. Lastly, since no solvent effects on the fluorescence yields and lifetimes of 1-methyl- and 1-methylallyl-2-pyridone were observed, we assume that the rates for all additional modes of radiationless decay from IBP<sup>s1</sup> ( $k_d$ ) are solvent polarity invariant.<sup>7</sup> The exact nature of the decay process measured by  $k_d$  is not known.

On the basis of these data it appears reasonable to ascribe the observed changes in  $\phi_f$  and  $\tau$

$$\phi_f = \frac{k_f}{k_c + k_f + k_{DP} + k_d} = k_f \tau \quad (1)$$

to an effect of solvent polarity on the rate constant for ylide formation,  $k_c$ . The effects of solvent polarity on  $k_c$  can be analyzed quantitatively using the solvent associated linear free-

**Figure 1.**

energy treatment suggested by Grunwald and Winstein.<sup>8</sup> The relationship as applied to cyclization is given in

$$\log k_c = mY + \log k_{c0} \quad (2)$$

where  $k_c$  and  $k_{c0}$  are the ylide-formation rate constants in H<sub>2</sub>O-EtOH solutions and 20% (v/v) H<sub>2</sub>O-EtOH, respectively,  $m$  is the reaction parameter measuring the sensitivity of  $k_c$  to changes in solvent polarity, and  $Y$  is the solvent polarity parameters. Substitution for  $k_c$  in terms of  $\phi_f$  gives

$$\log \left( \frac{1}{\phi_f} - c \right) = mY + \log \left( \frac{1}{\phi_{f0}} - c \right) \quad (3)$$

where  $c = 1 + (k_d + k_{DP})/k_f$ . Data for the fluorescence yields of IBP in ethanol-water mixtures were analyzed according to eq 3 using nonlinear least-squares methods in which  $c$  and  $m$  are varied to give the best fit. An exceptionally close fit (Figure 1) of  $\phi_f$  to  $Y$  was found when  $c = 63.9 \pm 0.1$  and  $m = 0.49 \pm 0.07$ , a value for the latter which suggests that a significant degree of charge separation has developed at the transition state for ylide formation.<sup>8</sup> In a more qualitative vein, this treatment suggests that  $k_c$  increases by greater than two orders of magnitude when solvent is changed from EtOH to H<sub>2</sub>O.

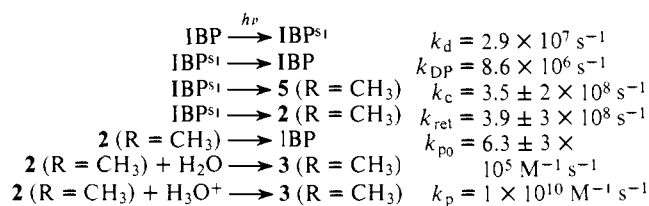
The increase in the photocyclization reaction efficiency of IBP with increasing [HClO<sub>4</sub>] noted in Table II must be due mainly to an enhanced rate for ylide trapping by hydronium ion. This feature has allowed us to obtain the exact unimolecular rate constants for IBP<sup>s1</sup> cyclization ( $k_c$ ) and ylide return to IBP<sup>s0</sup> ( $k_{ret}$ ), and the bimolecular rate constant for protonation of the ylide by water ( $k_{p0}$ ). Accordingly, nonlinear least-squares analysis of  $\phi_r$  vs. [H<sub>3</sub>O<sup>+</sup>] according to

$$\frac{1}{\phi_r} = \frac{1}{\tau k_c} + \frac{k_{ret}}{\tau k_c} \left[ \frac{1}{k_{p0}[\text{H}_2\text{O}]^+ + k_p[\text{H}_3\text{O}^+]} \right] \quad (4)$$

(which is easily derived using the kinetic sequence shown in Chart I) is performed by varying  $k_c$ ,  $k_{ret}$ , and  $k_{p0}$  to obtain the best fit. The values obtained for these rate constants are included in Chart I. The only assumption employed in this analysis is that the rate of proton transfer from H<sub>3</sub>O<sup>+</sup> to **2** is diffusion controlled ( $k_p = k_{diff} = 1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>), a reasonable expectation<sup>9</sup> based upon a predicted pK<sub>a</sub> of the pyridinium salt **3** (R = CH<sub>3</sub>) in the range of 10.<sup>10</sup>

The results presented above exemplify in a dramatic way the wealth of information that is available from a complete kinetic analysis of the 1-vinyl-2-pyridone photochemical and photophysical properties. Thus, rate constants for all processes initiating from IBP<sup>s1</sup>, with perhaps the exception of  $k_d$ , have been obtained. Although the inaccuracies inherent in measurements of  $\tau$  and  $k_c$  prevent a direct determination of  $k_d$  as  $1/\tau - k_f - k_c - k_{DP}$ , an estimate of  $2.9 \times 10^7$  s<sup>-1</sup> can be made

Chart I



using the derived values for  $c$  (from the solvent polarity treatment) and  $k_{\text{DP}}$ . A summary of all of the room temperature rate constants in water is given in Chart I.

**Acknowledgments.** Financial support of this research initially by the National Institutes of Health (CA-16695) and currently by the Robert A. Welch Foundation and the Department of Energy is acknowledged. We express our appreciation for the assistance given us by Professors Janos Fendler and Michael Hall in performing photophysical measurements and statistical analyses.

## References and Notes

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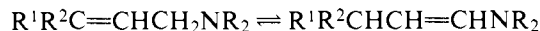
Received December 12, 1977

## Metal-Assisted Terpenoid Syntheses. 6.<sup>1</sup> Enantioselective Hydrogen Migration in Prochiral Allylamine Systems by Chiral Cobalt Catalysts

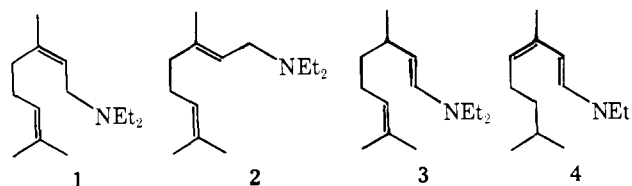
Sir:

Transition metal catalyzed double-bond migration has been extensively studied.<sup>2</sup> The isomerization products obtained with efficient catalysts generally reflect thermodynamic control implying effective reversibility of the reaction steps involved. Therefore migration of a multisubstituted inner double bond of an olefin to the less-substituted terminal one would not be possible unless the latter gains relative stability.<sup>3</sup> We are interested in transition metal catalyzed isomerization of substituted allylamines to the corresponding enamines, as the isomerization of prochiral allylamines poses an interesting problem of enantioselection. Organic base catalysts were reported<sup>4-8</sup> to be effective only for unsubstituted allylamines ( $R_1, R_2 = \text{H}$ ), and neither the transition metal catalysis nor the

stereospecific reaction has been reported for the isomerization of substituted allylamines. We wish to report here an enantioselective isomerization of prochiral allylamines to chiral enamines, an aldehyde equivalent, a stereospecific hydrogen migration reaction which has never been observed in the entire field of olefin catalysis.



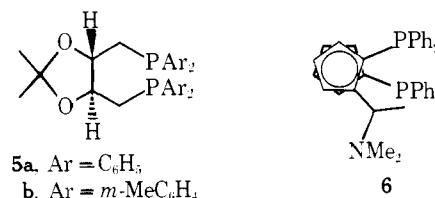
For the nonstereospecific isomerization, a discrete compound  $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$ <sup>9</sup> was found to be effective. For example, *N,N*-diethylpropenylamine (*N,N*-diethyl-3-methyl-2-butenylamine) was isomerized with 1 mol % of the complex (80 °C, 15 h, THF) to give 95% isolated yield of the *trans*-propenylamine (*N,N*-diethyl-3-methyl-1(*E*)-butenylamine). Similarly, *N,N*-diethylnerylamine<sup>10</sup> (**1**) and *N,N*-diethylgeranylamine<sup>11</sup> (**2**) were isomerized to give the racemic citronellal-*trans*-enamine<sup>12</sup> (**3**) in 85% yield together with a small amount (<15%) of the 1,3-dienamine<sup>13</sup> (**4**).



More conveniently, a cobalt catalyst is prepared in situ from cobalt(II) salts, e.g., naphthenate,<sup>14</sup> with  $\text{AlEt}_3$  or  $\text{AlH}(i\text{-Bu})_2$ , and  $\text{PPh}_3$  (mol ratio, 1:3:3). Comparable yields and similar or slightly higher reaction rates were obtained as compared to  $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$ . The enantioselective reaction was effected with this Ziegler type catalyst employing a chiral phosphorus ligand in place of  $\text{PPh}_3$ .

Monodentate chiral ligands L gave low optical yields for isomerization of **1**. A reaction solution (50:1:3:3 **1**/Co/L/ $\text{AlH}(i\text{-Bu})_2$ , L =  $\text{Ph}_2\text{P}(O\text{-menthyl})$ <sup>15</sup> or  $\text{Ph}_2\text{P}\text{-menthyl}$ <sup>16</sup>) gave (80 °C, 15 h, THF) (3*R*)-**3** (~20% yield) in 7% ee.<sup>17</sup> Similarly the catalysts prepared with  $\text{Ph}_2\text{P}(\text{neo-menthyl})$ <sup>18</sup> and (*S*)- $\text{PhP}(O\text{-}o\text{-MeC}_6\text{H}_4)\text{Me}$ <sup>19</sup> gave (3*S*)-**3** (20 and 5% yield, respectively) in ~5% ee<sup>17</sup> for both cases.

Chiral diphosphines gave better optical yields for the isomerization of **1** and **2**. Thus the reaction of **1** was effected (60 °C, 64-75 h, THF) with the cobalt catalyst prepared from (+)-diop<sup>20</sup> (**5a**) (50:1:1:3 **1**/Co/diop/ $\text{AlH}(i\text{-Bu})_2$ ) to give (3*R*)-**3** (23% yield) in 32% ee. Under the same conditions, the isomerization of **2** gave (3*S*)-**3** (12% yield) in 33% ee. Several



other chiral diphosphines were tested. A modified (+)-diop (**5b**) having a methyl group at a meta position of the phenyl groups did not improve the enantioselectivity. Substitution of the  $\text{PPh}_2$  groups of (+)-diop with  $\text{AsPh}_2$  reduces both the catalytic activity and the enantioselectivity. (*R,S*)-Aminoethylferrocenyldiphosphine<sup>21</sup> (**6**) is known as a chiral ligand capable of forming a highly enantioselective rhodium(I) hydrogenation catalyst.<sup>21</sup> A cobalt catalyst prepared with this ligand isomerized **1** (50:1:1:3 **1**/Co/**6**/ $\text{AlH}(i\text{-Bu})_2$ ) at 70 °C for 50 h into (3*R*)-**3** (10% yield) in 10% ee, but, at 90 °C for 50 h, **1** was isomerized into (3*S*)-**3** (50% yield) in 17% ee. This reversal in the product configuration and unusual increase in optical yield perhaps reflect the configurational flexibility of the ligand.