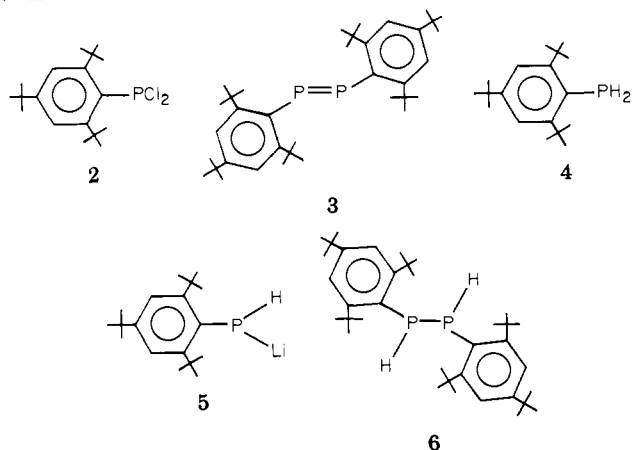


Chart I



prompted to reinvestigate the reaction of **2** with Mg in THF. We find that this is not a straightforward reaction.  $^{31}\text{P}\{^1\text{H}\}$  peaks are detectable at +494 and -64 ppm. In proton-coupled experiments the +494-ppm peak remained a singlet, while the one at -64 ppm became a six-line AA'XX' pattern. The -64-ppm peak, therefore, cannot correspond to the P=P bonded compound, **3**. Confirmation that the  $^{31}\text{P}$  chemical shift of **3** is, in fact, +494 ppm was provided by dissolving crystals with properties identical with those of **3** in  $\text{CH}_2\text{Cl}_2$  and recording both  $^{31}\text{P}\{^1\text{H}\}$  and  $^{31}\text{P}$  NMR spectra.

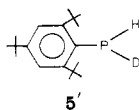
We turn next to the identity of the material responsible for the -64-ppm peak (-59 ppm as reported by Yoshifuji et al.<sup>3</sup>). Reduction of **2** with  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  solution affords high yields of the primary phosphine **4**, mp 144 °C. NMR data for **4** are as follows:  $^{31}\text{P}$  NMR (36.43 MHz)  $\delta$  -132 (t,  $J_{\text{PH}} = 209$  Hz);  $^1\text{H}$  NMR (90 MHz) *p-t*-Bu (s, 9 H,  $\delta$  1.32), *o-t*-Bu (s, 18 H,  $\delta$  1.60), P-H (d, 2 H,  $\delta$  4.22  $J_{\text{PH}} = 209$  Hz), C-H (d, 2 H,  $\delta$  7.52,  $J_{\text{PCCCH}} = 2.3$  Hz). Treatment of **4** with *n*-BuLi results in the monolithio species<sup>11,12</sup> **5**, which is responsible for a solvent-dependent doublet in  $^{31}\text{P}$  NMR spectra: THF (d,  $\delta$  -110,  $J_{\text{PH}} = 171.8$  Hz),  $\text{Et}_2\text{O}$  (d,  $\delta$  -125,  $J_{\text{PH}} = 189.0$  Hz). The reaction of **5** with  $\text{CCl}_4$  affords 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphine (**6**) in virtually quantitative yield.<sup>13</sup> The  $^{31}\text{P}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **6** are identical with those recorded for reaction mixtures of **2** and Mg in THF.  $^1\text{H}$  NMR data (90 MHz) for **6** are as follows: *p-t*-Bu (s, 18 H,  $\delta$  1.3), *o-t*-Bu (s, 36 H,  $\delta$  1.4), P-H (AA'XX' pattern, 2 H,  $\delta$  4.7,  $J_{\text{PH}} = 221.0$ ,  $J_{\text{PP}} = 192.4$ ,  $J_{\text{PPH}} = 16.0$ ,  $J_{\text{HPPH}} = 1.0$  Hz). In summary, the reaction of **2** with Mg in THF results inter alia in **3** and **6**. The  $^{31}\text{P}$  chemical shift of the diphosphene **3** should be +494 ppm and not -59 ppm as reported by Yoshifuji et al.<sup>3</sup> The compound responsible for the -59-ppm  $^{31}\text{P}$  NMR peak is, in fact, the diphosphine **6**, which can be regarded as the product of oxidative addition of  $\text{H}_2$  to the P=P bond.

(9) For a summary of  $^{31}\text{P}$  NMR data on phosphalkenes, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731-744 and references therein.

(10) The only phosphalkene with a negative  $^{31}\text{P}$  chemical shift is  $\text{HP}=\text{CF}_2$ .<sup>9</sup>

(11) Compound **4** undergoes monolithiation even if excess *n*-BuLi, *n*-BuLi/TMEDA, MeLi (-60 °C), or KH is employed. Presumably this is due to the steric bulk of the 2,4,6-tri-*tert*-butylphenyl group. Interestingly, however, the sterically congested phosphine<sup>4</sup>  $(\text{Me}_3\text{Si})_3\text{CPH}_2$  will undergo dilithiation with *n*-BuLi.

(12) Further proof that **4** undergoes only monolithiation was provided by  $\text{D}_2\text{O}$  quenching of **5**, which results in **5'**:  $^{31}\text{P}$  NMR ( $\text{Et}_2\text{O}$ ) (d of t,  $\delta$  -133,  $J_{\text{PH}} = 189.0$ ,  $J_{\text{PD}} = 32.2$  Hz).



(13) A variety of other chlorinated compounds will convert **5** to **6**, e.g., *t*-BuPCl<sub>2</sub>, and PCl<sub>3</sub>. Presumably, the mechanism involves lithium-chlorine exchange.

The reactivity of **1**<sup>14</sup> and theoretical aspects<sup>15</sup> of the phosphorus-phosphorus double bond are under active investigation.

**Acknowledgment.** Generous financial support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is gratefully acknowledged.

**Registry No.** **1**, 83115-11-1; **2**, 79074-00-3; **3**, 79073-99-7; **4**, 83115-12-2; **5**, 83115-13-3; **6**, 83115-14-4;  $(\text{Me}_3\text{Si})_3\text{PCl}_2$ , 75235-85-7;  $(\text{Me}_4\text{Si})_3\text{Cl}$ , 28830-22-0; sodium naphthalene, 3481-12-7.

(14) Preliminary NMR studies reveal that **1** exhibits short-term stability with respect to water and oxygen. Solutions of **1** in organic solvents degrade over a number of hours as evidence by the appearance of new  $^{31}\text{P}$  NMR peaks between +20 and +40 ppm.

(15) The model diphosphene  $\text{HP}=\text{PH}$  has been investigated by ab initio molecular orbital calculations. Boggs, J. E.; Cowley, A. H.; Lee, J.-G., to be submitted for publication.

### Cis Selectivity of "Salt-Free" Wittig Reactions: A "Leeward Approach" of the Aldehyde at the Origin

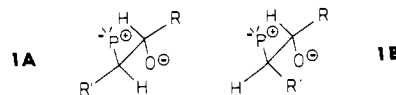
Manfred Schlosser\* and Bruno Schaub

*Institut de Chimie organique de l'Université  
CH-1005 Lausanne, Switzerland*

*Received April 28, 1982*

Despite its great practical importance, the cis selectivity<sup>1</sup> encountered in Wittig olefin syntheses with "salt-free" triphenylphosphonio ylides and aldehydes has not yet found a conclusive explanation. The conformational analysis presented in this communication provides a new and successful approach to solve this question.

First efforts<sup>2</sup> of rationalization invoked an anti-periplanar alignment of the combining PC and CO dipoles. The three intermediate (**1B**) should then suffer from the gauche interaction



of two organic groups ( $\text{R} = \text{alkyl}$  or aryl,  $\text{R}' = \text{alkyl}$ ) and consequently the erythro stereoisomer (**1A**) would be produced preferentially. But not only did the basic assumption, the anti-periplanar orientation, remain unsubstantiated, also the magnitude of cis selectivity could hardly be understood on the basis of such conformational effects.<sup>3</sup>

The next attempts<sup>4</sup> to deal with the problem postulated an unprecedented geometry of the adduct-generating transition state. The aldehyde was thought to approach the ylide in a plane perpendicular to that occupied by the ylide center to minimize steric repulsions. The formyl hydrogen would, of course, point toward the ylide (**2A**). In the moment of carbon-carbon linking, it would turn away from the bulky alkyl group  $\text{R}'$ , thus imposing a cis relationship on the groups  $\text{R}$  and  $\text{R}'$ . The concept of the perpendicular approach became popular when oxaphosphetanes were recognized to be generally the only metastable intermediates in Wittig reactions.<sup>5</sup> This orientation (transition state **2B** or **2C**)

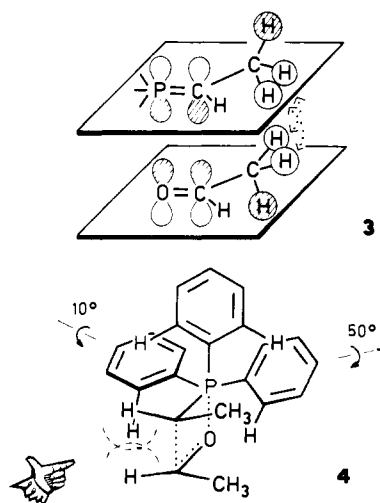
(1) (a) Schlosser, M.; Christmann, K. F. *Justus Liebigs Ann. Chem.* **1967**, *708*, 1. (b) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1.

(2) (a) Bergelson, L. D.; Shemyakin, M. M. *Angew. Chem.* **1964**, *76*, 113; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 250. (b) Rüdhardt, C.; Panse, P.; Eichler, S. *Chem. Ber.* **1967**, *100*, 1144.

(3) Reference 1a, pp 17-18.

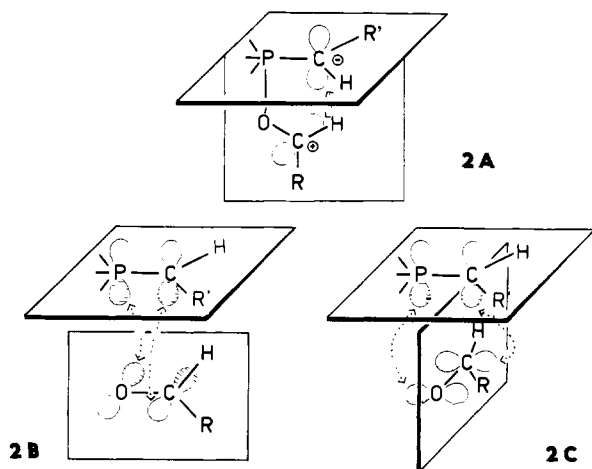
(4) (a) Schneider, W. P. *Chem. Commun.* **1969**, 785. (b) Schlosser, M.; Heinz, G. *Angew. Chem.* **1968**, *80*, 849; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 820.

(5) (a) Vedejs, E.; Snoble, K. A. *J. Am. Chem. Soc.* **1973**, *95*, 5778. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. *J. Am. Chem. Soc.* **1981**, *103*, 2823. (c) As specified in ref 5b, these authors, however, favor a tilted over a plane-parallel transition state mainly for stereochemical (i.e., geometrical) rather than for orbital symmetry reasons.



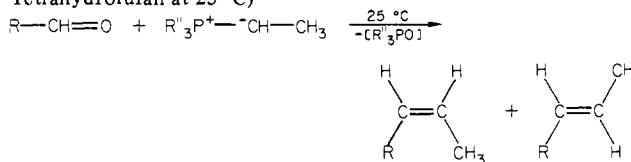
would allow an aldehyde, but not a ketone, to perform with an ylide a  $[\pi_2s + \pi_2a]$  cycloaddition leading immediately to the oxaphosphetane, without need for a zwitterionic precursor and without violation of orbital symmetry rules.<sup>5</sup>

Finally, in a kind of emergency solution, Van der Waals attractive forces were suggested to bring about the mysterious *cis* selectivity.<sup>1b,6</sup> This hypothesis also attained the sanctification of orbital symmetry considerations. Hyperconjugative  $\sigma(\sigma^*)/p$  mixing may induce matching symmetries at the groups R and R', giving rise to a secondary stabilizing interaction (3).<sup>7</sup>



Such a steric attraction,<sup>7</sup> whatever its true nature may be, should accelerate the reaction. When we studied the relative rates with which ylides and aldehydes combine, we found, however, that *cis*-oxaphosphetane was generated at an ordinary rate, whereas formation of the *trans* isomer turned out to be seriously hindered.<sup>8,9</sup> We argued that this must be a result of steric crowding and, upon

Table I. Yields and, in Parentheses, *Cis/Trans* Ratios of Olefins Obtained from Wittig Reactions between Aldehydes and (Triphenylphosphonio)- or (Triethylphosphonio)ethylide (in Tetrahydrofuran at 25 °C)



	yield, % ( <i>Z/E</i> ratio)	
	R'' = phenyl	R'' = ethyl
R = hexyl	95 (86:14)	94 (33:67)
R = <i>tert</i> -butyl	92 (98:2)	92 (10:90)
R = phenyl	94 (87:13)	99 (17:83)
R = <i>p</i> -chlorophenyl	88 (88:12)	89 (4:96)

inspection of Dreiding models,<sup>10</sup> found evidence for this assumption. At the transition state (4) of oxaphosphetane formation all three "stationary"<sup>11</sup> phenyl rings are nearly immobilized. The alkyl group R' (in 4, CH<sub>3</sub>) forces the neighboring phenyl ring out of the plane given by the phosphorus trigonal basis by roughly 50°. The axial phenyl is confined to a perpendicular orientation with respect to the four-membered ring. The third phenyl substituent is only slightly twisted out of the pyramidal plane (by roughly 10°) and points with an *o*-hydrogen atom right toward one of the substituents flanking the carbonyl group. Thus, any bulky group on this face of the future oxaphosphetane ring must cause serious steric repulsions. In contrast, on the opposite side the substituent R (in 4, CH<sub>3</sub> again) may approach "leeward" of the ylide side-chain R', which has pushed the neighboring phenyl ring out of way.

If these conclusions are correct, ylides with sterically less demanding "stationary groups" should no longer exhibit *cis* but rather *trans* selectivity. This prediction was confirmed in a series of experiments conducted with "salt-free" (triethylphosphonio)ethylide.<sup>11</sup> Upon its tetrahydrofuran solution being mixed with aldehydes at -75 °C, the adducts were formed almost instantaneously and essentially irreversibly (i.e., without any significant subsequent stereoisomerization).<sup>8</sup> After 2–4 h at 25 °C the olefins were obtained with high yields and predominant *trans* configuration (see Table I).

Although referring only to a transition state, model 4 suggests that also in the ground state a *cis*-disubstituted oxaphosphetane may be sterically less congested and hence thermodynamically more stable than its *trans* isomer. This appears to be the case indeed. At 0 °C, the *cis* adduct obtained from (triphenylphosphonio)ethylide and benzaldehyde sets free the olefin at half the rate compared with its *trans* isomer. On the other hand, the corresponding *cis*-oxaphosphetane derived from (triethylphosphonio)ethylide decomposes at 25 °C 5 times more rapidly than its *trans* isomer.<sup>8,12</sup> In addition, model 4 can account for several unexplained features of the Wittig reaction: the decrease in *cis* selectivity upon branching of the ylide side chain, whereas branching of the aldehyde leads to an increase;<sup>1b</sup> the puzzling *Z* selectivity observed with  $\alpha$ -alkoxy ketones<sup>13</sup> (the ether oxygen atom can interact with the phosphorus atom only when approaching the twisted phenyl ring); and last not least, the high *trans* selectivity of ylides derived from tributylvinylphosphonium bromide.<sup>14</sup>

(6) Schlosser, M. *Bull. Soc. Chim. Fr.* 1971, 453.

(7) Hoffmann, R.; Levin, C. C.; Moss, R. A. *J. Am. Chem. Soc.* 1973, 95, 629.

(8) Schaub, B.; Piskala, A.; Rehan, A. H.; Respondek, J.; Schlosser, M., details to be published elsewhere.

(9) These relative reactivities of (triphenylphosphonio)propylide vs. -methylide were found in competition experiments: 3.1 when reacted with an insufficient amount of formaldehyde, 1.9 and 0.12 with benzaldehyde depending on whether *cis*- or *trans*-oxaphosphetane was formed. The aldehydes were added dropwise to a mixture of (triphenylphosphonio)methylide and -propylide (molar ratios 1:1:1) in tetrahydrofuran at -75 °C. The yields and isomeric composition of olefins formed after 2 h at 25 °C were measured by gas chromatography (ethylene and 1-butene being distilled into a trap filled with a solution of bromine in dichloromethane and identified as the dibromides). The amounts of nonconsumed ylides were determined by reacting them with excess *p*-chlorobenzaldehyde. Similarly, solutions of (triphenylphosphonio)methylide or -propylide were added to a mixture of formaldehyde and benzaldehyde (molar ratios again 1:1:1). The latter reacted 3–4 times faster.

(10) All carbon centers equipped with the appropriate number of acrylic glass disks simulating the Van der Waals radii of hydrogen atoms.

(11) (a) Köster, R.; Simic, D.; Grassberger, M. A. *Justus Liebigs Ann. Chem.* 1970, 739, 211. (b) Schmidbaur, H.; Tronich, W. *Chem. Ber.* 1968, 101, 595.

(12) The oxaphosphetanes were prepared at -75 °C in tetrahydrofuran. After thermostating, samples were drawn in intervals. Having determined the concentrations of *cis*- and *trans*-1-phenylpropene they contained (99% at "infinite" time), we calculated the amounts of remaining *cis*- and *trans*-oxaphosphetanes.

(13) Sreekumar, C.; Darst, K. P.; Still, W. C. *J. Org. Chem.* 1980, 45, 4260.

(14) Meyers, A. I.; Lawson, J. P.; Carver, D. R. *J. Org. Chem.* 1981, 46, 3119.

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**Registry No.** (Z)-2-Nonene, 6434-77-1; (E)-2-nonene, 6434-78-2; (Z)-4,4-dimethyl-2-pentene, 762-63-0; (E)-4,4-dimethyl-2-pentene, 690-08-4; (Z)-1-phenyl-1-propene, 766-90-5; (E)-1-phenyl-1-propene, 873-66-5; (Z)-1-(p-chlorophenyl)-1-propene, 1879-52-3; (E)-1-(p-chlorophenyl)-1-propene, 1879-53-4; heptanal, 111-71-7; 2,2-dimethylpropanal, 630-19-3; benzaldehyde, 100-52-7; p-chlorobenzaldehyde, 104-88-1; triphenylethylidene phosphorane, 1754-88-7; triethylethylidene phosphorane, 17847-85-7.

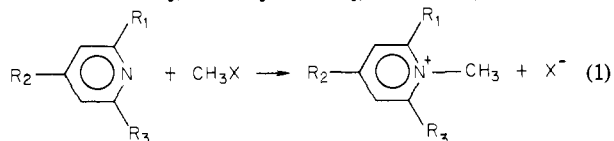
### An Inverse Reactivity-Selectivity Relationship. Kinetic Nitrogen Isotope Effects on Methyl Transfer to Pyridines

Joseph L. Kurz\* and Moheb M. Seif El-Nasr

Department of Chemistry, Washington University  
St. Louis, Missouri 63130  
and Department of Chemistry, Lindenwood Colleges  
St. Charles, Missouri 63301

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We report that values of the  $^{14}\text{N}/^{15}\text{N}$  rate constant ratio for methyl transfer to alkyl-substituted pyridines (eq 1:  $\text{R}_1, \text{R}_2, \text{R}_3 = \text{H}, \text{H}, \text{H}; \text{H}, \text{CH}_3, \text{H}; \text{CH}_3, \text{H}, \text{CH}_3$ ) decrease (become more



inverse) as  $\text{CH}_3\text{X}$  becomes more reactive and may also decrease as the pyridine becomes more reactive. Numerical values are given in Table I.

These changes in  $k_{14}/k_{15}$  demonstrate increasing selectivity for  $^{15}\text{N}$  in preference to  $^{14}\text{N}$  as reactivity increases and thus are in violation of the reactivity-selectivity principle.<sup>1</sup> They also are in violation of commonly accepted rules concerning the effects of substituents on transition-state structures; those rules predict that increases in reactivity that result from changes in the leaving group (or, with less certainty, in the nucleophile) will decrease the N-CH<sub>3</sub> bond order in the transition state.<sup>2</sup> Such a decrease in N-CH<sub>3</sub> bonding would make  $k_{14}/k_{15}$  less inverse.

However, these observed changes in  $k_{14}/k_{15}$  are consistent with a very recent prediction by Pross and Shaik<sup>3</sup> that such "anti-Hammond" effects should result from changes in quantum mechanical mixing of configurations in the transition state and should, when comparisons are made within a limited family of reactions, dominate the more familiar effects of structural perturbations of the free energy surface.

The reactions were run in aqueous acetonitrile (10% acetonitrile, 0.96 mol fraction of water). The nucleophile was in excess, and the reactions were run to completion; thus the fraction of reaction for the nitrogen is given by the initial  $\text{CH}_3\text{X}/\text{nucleophile}$  ratio.<sup>4</sup>

\* To whom correspondence should be addressed at Washington University.

(1) For reviews of the reactivity-selectivity principle, see: (a) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69-126. (b) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755-765.

(2) For recent discussions of the application of such arguments to  $\text{S}_{\text{N}}2$  reactions, see: (a) Harris, J. M.; Shafer, S. G.; Moffat, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295-3300. (b) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper & Row: New York, 1981; Chapters 2, 4.

(3) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702-3709.

Table I. Values of  $k_{14}/k_{15}$  at 25 °C<sup>a</sup>

nucleophile <sup>b</sup>	$\text{CH}_3\text{X}^c$		
	$\text{CH}_3\text{I}$	$\text{CH}_3\text{OTs}$	$\text{CH}_3\text{OTf}$
2,6-Me <sub>2</sub> py	1.004 ± 0.002 <sup>d</sup>	1.000 ± 0.002 <sup>e</sup>	0.986 ± 0.002 <sup>f</sup>
py	1.001 ± 0.001 <sup>d</sup>	1.001 ± 0.002 <sup>e</sup>	0.976 ± 0.001 <sup>f, h</sup> 0.976 ± 0.001 <sup>g, h</sup>
4-Me(py)	1.001 ± 0.001 <sup>d</sup>	0.993 ± 0.002 <sup>e</sup>	0.972 ± 0.005 <sup>f</sup>

<sup>a</sup> Solvent is 10% (v/v)  $\text{CH}_3\text{CN}$  in  $\text{H}_2\text{O}$ . Temperature uncertainty is ca. ± 0.1 °C for reactions of  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{OTs}$ , ca. ± 1 °C for reactions of  $\text{CH}_3\text{OTf}$ . Uncertainties are standard deviations of the listed means of ratios from two or more separate experiments. <sup>b</sup> 2,6-Me<sub>2</sub>py is 2,6-dimethylpyridine; py is pyridine; 4-Me(py) is 4-methylpyridine. <sup>c</sup>  $\text{CH}_3\text{OTs}$  is methyl *p*-toluenesulfonate,  $\text{CH}_3\text{OTf}$  is methyl trifluoromethanesulfonate.

<sup>d</sup>  $[\text{Nucleophile}]_0 = 0.50 \text{ M}$ ;  $[\text{CH}_3\text{I}]_0 = 0.010 \text{ M}$ .

<sup>e</sup>  $[\text{Nucleophile}]_0 = 0.25 \text{ M}$ ;  $[\text{CH}_3\text{OTs}]_0 = 0.0050 \text{ M}$ .

<sup>f</sup>  $[\text{Nucleophile}]_0 = 0.010 \text{ M}$ ;  $[\text{CH}_3\text{OTf}]_0 = 0.0010 \text{ M}$ . <sup>g</sup>  $[\text{py}]_0 =$

$0.0016 \text{ M}$ ;  $[\text{CH}_3\text{OTf}]_0 = 0.00040 \text{ M}$ . <sup>h</sup> The observation that

$k_{14}/k_{15}$  is independent of  $[\text{py}]_0$  for py +  $\text{CH}_3\text{OTf}$  verifies that

our mixing time was short in comparison to the half-time for

this reaction; for all runs using  $\text{CH}_3\text{OTf}$ , a solution of  $\text{CH}_3\text{OTf}$

in  $\text{CH}_3\text{CN}$  was injected into a rapidly stirred solution of the

nucleophile.

The  $^{15}\text{N}/^{14}\text{N}$  ratio in the product was measured by an adaption of a known procedure.<sup>5</sup> The methylpyridinium ion was isolated as the tetraphenylborate salt and purified by recrystallization, and its nitrogen was converted to  $\text{N}_2$ .<sup>6</sup> The  $^{15}\text{N}/^{14}\text{N}$  ratio in the  $\text{N}_2$  was then measured by using a Micromass 602E isotope-ratio mass spectrometer. The  $^{15}\text{N}/^{14}\text{N}$  ratio in the reactant was determined by a parallel procedure in which the pyridine first was converted quantitatively into the methylpyridinium ion by reaction with excess  $\text{CH}_3\text{X}$ . The  $k_{14}/k_{15}$  isotopic rate constant ratio was calculated as described by Melander and Saunders<sup>7</sup> from these two  $^{15}\text{N}/^{14}\text{N}$  ratios and the fraction of reaction.

Values of "bond-formation" kinetic isotope effects such as these are products of two factors: a "normal" (tending to make  $k_{14} > k_{15}$ ) factor, which is equal to the isotopic ratio of imaginary frequencies for motion along the reaction coordinate, and an "inverse" (tending to make  $k_{14} < k_{15}$ ) factor, which arises from bond formation to the isotopic atom.<sup>8</sup> This inverse factor directly measures the selectivity for  $^{15}\text{N}$  in preference to  $^{14}\text{N}$  and should become more inverse as the N-CH<sub>3</sub> bond order in the transition state increases. The normal (frequency ratio) factor can be shown to decrease toward unity as that N-CH<sub>3</sub> bond order increases.<sup>9,10</sup> Thus both factors which contribute to the observed  $k_{14}/k_{15}$  isotopic selectivity ratio should be simply related to the N-CH<sub>3</sub> bond order in the transition state: A sufficiently low N-CH<sub>3</sub> bond order should give  $k_{14}/k_{15} > 1$ , a sufficiently high N-CH<sub>3</sub> bond order should give  $k_{14}/k_{15} < 1$ , and decreasing values of  $k_{14}/k_{15}$  (observed here as reactivity increases) should accompany increasing N-CH<sub>3</sub> bonding in the transition state.

The order of increasing reactivity of  $\text{CH}_3\text{X}$  is  $\text{CH}_3\text{I} < \text{CH}_3\text{O}-\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3 \ll \text{CH}_3\text{OSO}_2\text{CF}_3$ .<sup>11</sup> Table I shows that selectivity

(4) Corrections of this fraction for the effect of the competing reaction of  $\text{CH}_3\text{X}$  with water were required only for the reactions of  $\text{CH}_3\text{OTf}$ . Uncertainties in these corrections are too small to affect the observed ordering of the  $k_{14}/k_{15}$  values.

(5) Shearer, G. B.; Kohl, D. H.; Commoner, B. *Soil Sci.* **1974**, *118*, 308-316.

(6) The Kjeldahl digestion in ref 5 was modified as described by Fish and Collier (Fish, U. B.; Collier, P. R. *Anal. Chem.* **1958**, *30*, 151-152) in order to achieve quantitative conversion of the pyridinium nitrogen.

(7) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley-Interscience: New York, 1980; p 100.

(8) Fry, A. In "Isotope Effects in Chemical Reaction"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: Princeton, 1970; Chapter 6.

(9) Bigeleisen, J.; Wolfsberg, M. *J. Chem. Phys.* **1954**, *22*, 1264; Figure 1, Curve 7.

(10) Reference 7, pp 315-318.

(11) The relative reactivities are  $\text{CH}_3\text{I}:\text{CH}_3\text{OTs}:\text{CH}_3\text{OTf} = 1:10:\sim 10^5$ . This  $\text{CH}_3\text{I}:\text{CH}_3\text{OTs}$  ratio is from conductimetric rate measurements in dilute aqueous solution which gave 10.3 and 9.5 for pyridine and 4-picoline, respectively.<sup>12</sup> This  $\text{CH}_3\text{OTs}:\text{CH}_3\text{OTf}$  ratio is estimated from the corresponding hydrolysis rates in aqueous solution.<sup>13,14</sup>