a simple dissociative path where metaphosphate monomer escapes from the encounter complex and has a significant lifetime. The data do not fit any curve of the family predicted from the theoretical equation of the stepwise process; since the equation is normalized, the horizontal position of a member of the family of curves is fixed by the pK of the donor pyridine and only the vertical position varied to fit the experimental data. The limiting slope of the curve predicted for the stepwise mechanism is reasonably expected to be similar to the β for the attack of pyridines on phosphoramidate (+0.2) where expulsion of ammonia from the preassociation complex would be rate determining. The theoretical line for $\beta_N = 0.2$ is shown fitting the points at high pK where close examination suggests a limiting rate constant. This line deviates grossly from the low pK points (as illustrated), and fitting the same line (by vertical displacement) to the low pK points yields similar deviations for those at high pK. Curvature for β_N values higher than 0.2 is very pronounced (see the following paper[5]) and would be clearly visible in the data. A nontheoretical "curve" may be fitted to the data, but this necessitates a break at a pK ($\sim$7) that is not theoretically possible as the system is chosen so that the stepwise process, if operating, would be symmetrical at the pK of isoquinoline (5.42). Force fitting the theoretical equation for the stepwise process gives a best fit to a least-squares program where $\beta_N = 0.3$. The "residuals" for this fitting possess a nonrandom variation with pK consistent with a poor fit unlike those for the linear equation (see figure), which have a random distribution.

Jameson and Lawlor[9] observed that morpholine, piperazine, piperidine, and piperazine monocation reacted with 4-methylpyridine-N-phosphonate with a reactivity range of 3-fold. These amines are close structural analogues of each other, and if the stepwise path were operating, the dissociative step involving formation of the ternary complex would be rate limiting because the amines are more powerful nucleophiles than is 4-methylpyridine.

The present results indicate an essentially constant transition-state structure for phosphonyl group transfer over a wide range of acceptor basicities. Data for the β_{EQ} for transfer of the phosphate between pyridines[10] taken with the present data point to weak charges on the pyridine nitrogens in the transition state similar to those in the analogous sulfonate group transfer.[5] The transition site is symmetrical.

There is incontrovertible evidence from trapping and reactivity studies[11] that discrete metaphosphorimidate intermediates are formed in some transfer reactions in aqueous solution. Conditions must therefore exist for a system involving a preassociation mechanism that bridges the gap between concerted and the $S_N1(P)$ process where the intermediate is free. This has yet to be demonstrated in monophosphate reactions although the zero Brønsted exponent[12] in the aminolysis of 2,4-dinitrophenyl phosphate is indicative of such a mechanism.

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Registry No. 3-Cyanopyridine, 100-54-9; 3-bromopyridine, 626-55-1; 3-chloropyridine, 626-60-8; 3-methoxycarbonylpyridine, 93-60-7; 3-acetylpyridine, 350-03-8; 3-formylpyridine, 500-22-1; 4-bromopyridine, 1120-87-2; 4-chloropyridine, 626-61-9; 3-cyanomethylpyridine, 6443-85-3; 4-formylpyridine, 872-85-5; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 3,5-dimethylpyridine, 591-22-0; 3,4-dimethylpyridine, 583-58-4; 4-morpholinopyridine, 2767-91-1; 4-aminopyridine, 504-24-5; 4-dimethylaminopyridine, 1122-58-3; isoquinoline-N-phosphonate, 85370-61-2; isoquinoline, 119-65-3; ammonium phosphoramidate, 18299-52-0.

(10) Bourne, N.; Williams, A., unpublished observations, 1983.
(11) (a) Westheimer, F. H. *Spec. Publ.—Chem. Soc.* **1957**, *No. 8*, 118. (b) Williams, A.; Douglas, K. T. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1454. (c) Williams, A.; Douglas, K. T., Loran, J. S. *Ibid.* **1975**, 1010.
(12) Kirby, A. J.; Varvoglis, A. G. *J. Chem. Soc. B* **1968**, 135.

Preassociation Concerted Mechanism for Sulfate Group ($-SO_3^-$) Transfer between Isoquinoline-N-sulfonate and Substituted Pyridines[1a]

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There has been much discussion of the existence of preassociation stepwise processes in phosphoryl group transfer reactions[1b,2,3] in particular in relation to the central role of this reaction in biochemistry. Transfer of the analogous sulfate group from a nitrogen or oxygen donor involving free sulfur trioxide in the ternary complex with donor and acceptor may occur;[1b] transfer reactions of this group ($-SO_3^-$) have biological importance in the initial steps of inorganic sulfate utilization.[4]

Studies of the reaction of pyridine-N-sulfonates with aryl oxide ions have established that the transition state is symmetrical[5] with little bonding between sulfur and the entering or departing atoms. Although the symmetrical transition state is consistent with the concerted transfer of the sulfate group, it is difficult to distinguish between concerted and stepwise preassociation mechanisms for this reaction.

A Brønsted-type study of the reaction of substituted pyridines with isoquinoline-N-sulfonate[6] should be able to diagnose a concerted preassociation mechanism (eq 1) from a stepwise preas-

$$^+\text{isq}{-}SO_3^- + \text{xpyr} \rightleftarrows [^+\text{iso}{-}SO_3^-\cdot\text{xpyr}] \rightarrow |\text{isq}\cdots SO_3\cdots\text{xpyr}|^\ddagger \rightarrow [\text{isq}\cdot{}^+\text{xpyr}{-}SO_3^-] \rightleftarrows \text{isq} + {}^+\text{xpyr}{-}SO_3^- \quad (1)$$

sociation mechanism (eq 2). The former mechanism predicts a substantially linear relationship, whereas the stepwise mechanism predicts a break at a pK corresponding to that of isoquinoline.

Isoquinoline-N-sulfonate was prepared by passing SO_3 in a carrier stream of nitrogen through a solution of isoquinoline in dichloroethane.[6] Reaction of isoquinoline-N-sulfonate with pyridines was measured spectrophotometrically at 350 nm in aqueous buffers at 25 °C and 0.1 M ionic strength. The reaction, followed at pHs between 7 and 8, obeys good pseudo-first-order kinetics and has the rate law $k_{obsd} = k_{buffer} + k_{H_2O} + k_{xpyr}[\text{xpyr}]$, where the pyridine reacts in its basic form as determined from measurements with the basic pyridines. General base catalysis is excluded by the use of hindered pyridines (see caption to Figure 1), and water and the buffers, which are composed of hindered amines, contribute to the background reaction. The experimental data are shown in the figure, and the second-order rate constants obey an excellent linear plot: $\log k_{xpyr} = (0.23 \pm 0.002)pK^{xpyr} - (1.92 \pm 0.04)$ ($r = 0.995$). The observation of a linear relationship excludes the preassociation stepwise process and is consistent with a concerted one.

The theoretical equation for the stepwise mechanism (eq 2) has

$$^+\text{isq}{-}SO_3^- + \text{xpyr} \rightleftarrows [^+\text{isq}{-}SO_3^-\cdot\text{xpyr}] \rightleftarrows [\text{isq}\cdot\text{xpyr}\cdot SO_3] \rightleftarrows [\text{isq}\cdot{}^+\text{xpyr}{-}SO_3^-] \rightleftarrows \text{isq} + {}^+\text{xpyr}{-}SO_3^- \quad (2)$$

the form $k = k_0/(1 + 10^{\Delta pK\beta_N})$ where $\Delta pK = pK^{isq} - pK^{xpyr}$ and k_0 is the overall rate constant when formation of ternary complex is rate limiting ($\Delta pK < 0$). When decomposition of the ternary complex is rate limiting ($\Delta pK > 0$), the Brønsted-type plot becomes linear with slope β_N. The insert to the figure (B) illustrates

(1) (a) We thank ICI Organics Division, the SERC for financial support, and Professor W. P. Jencks for disclosing his work prior to its publication. (b) Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.
(2) Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313.
(3) Buchwald, S. L.; Knowles, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1438.
(4) Roy, A. B. "The Enzymes", 3rd ed.; Academic Press: New York, 1971; Vol. 5, chapter 1.
(5) Hopkins, A.; Day, R. A.; Williams, A., submitted for publication in *J. Am. Chem. Soc.*
(6) The material had satisfactory analytical data.

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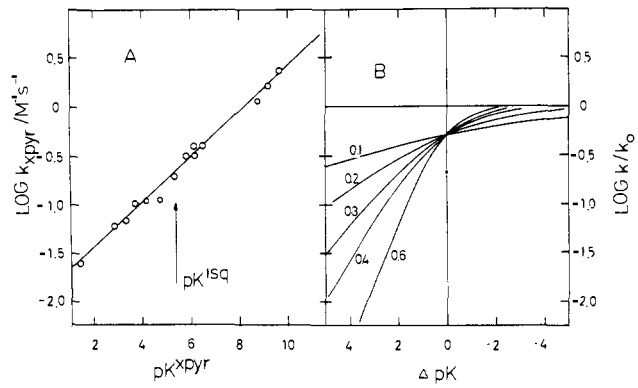

Figure 1. (A) Plot of log k_{xpyr} vs. pK^{xpyr} for the pyridinolysis of isoquinoline-*N*-sulfonate; 25 °C, 0.1 M ionic strength. The line is theoretical from the text; points in increasing value of pK^{xpyr}: 3-CN, 3-Br, 4-MeOCO, 3-CHO, 3-CH_2CN, 4-CHO, H, 3-Me, 3,5-Me_2, 4-Me, 3,4-Me_2, 4-morpholino, 4-NH_2, 4-Me_2N. General base catalysis is excluded by the observation that $k_{2,6\text{-lutidine}}$ ($10^{-2.4}$ M^{-1} s^{-1}) is some 2 orders of magnitude lower than that predicted from the Brønsted equation given in the text. (B) Family of normalized curves (log k/k_0) vs. ΔpK for the theoretical rate law governing a preassociation stepwise mechanism (eq 2). Numbers refer to the chosen value of β_N for the rate law.

a family of normalized curves for different values of β_N, and it is clear that none of these β_N values generates a theoretical curve to fit the data. The curves will only approximate to a straight line when $\beta_N < 0.1$. The data may be force fitted to the equation for the stepwise process and a best fit obtained to a least-squares program where $\beta_N = 0.4$. The correlation coefficient for this fit is quite good, but the residuals possess a nonrandom variation with pK, whereas those for the linear fit have a random distribution.

The conclusion of a preassociation concerted mechanism is very similar to that for the analogous pyridine-*N*-phosphonate transfer reactions.[7] The comparison extends to a similar reactivity and a low value of the bond order in the transition state as measured by the ratio of β_N to the value of β for the equilibrium ($\beta_N/\beta_{EQ} = 0.19$, $\beta_{EQ} = 1.24$[5]). The absence of free or solvated sulfur trioxide as an intermediate in solvolysis reactions in solvents of low water content[8] and of the preassociative stepwise mechanism are consistent with the known high reactivity of monomeric sulfur trioxide.[9] Analogues of sulfur trioxide such as sulfen,[10] aminosulfen (MeN=SO_2),[11] and paraoxosulfen (*p*-$OC_6H_4SO_2$)[12] are expected to be less reactive than sulfur trioxide and have been demonstrated as *discrete* intermediates in transfer reactions.[10-12] Since these "sulfen" intermediates (X=SO_2) exhibit a spectrum of reactivity, it is quite possible that an intermediate could be devised that would participate in a preassociation stepwise mechanism.

Registry No. Isoquinoline-*N*-sulfonate, 53854-50-5; 3-cyanopyridine, 100-54-9; 3-bromopyridine, 626-55-1; methyl 4-pyridinecarboxylate, 2459-09-8; 3-pyridinecarboxaldehyde, 500-22-1; 3-pyridineacetonitrile, 6443-85-2; 4-pyridinecarboxaldehyde, 872-85-5; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 3,5-dimethylpyridine, 591-22-0; 4-methylpyridine, 108-89-4; 3,4-dimethylpyridine, 583-58-4; 4-morpholinopyridine, 2767-91-1; 4-aminopyridine, 504-24-5; 4-dimethylaminopyridine, 1122-58-3; 2,6-lutidine, 108-48-5; sulfur trioxide, 7446-11-9.

(7) Bourne, N.; Williams, A., preceding paper in this issue.
(8) Hopkins, A.; Williams, A. *J. Chem. Soc., Chem. Commun.* **1983**, 37.
(9) (a) Gilbert, E. E. *Chem. Rev.* **1962**, *62*, 549. (b) The reactivity against nucleophiles of monomeric sulfur trioxide has to our knowledge never been measured but must be very much greater than that of the polymeric forms, which are themselves exceptionally reactive.
(10) Davy, M. B.; Douglas, K. T.; Loran, J. S.; Steltner, A.; Williams, A. *J. Am. Chem. Soc.* **1977**, *99*, 1196.
(11) Williams, A.; Douglas, K. T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1727.
(12) Thea, S.; Guanti, G.; Hopkins, A.; Williams, A. *J. Am. Chem. Soc.* **1982**, *104*, 1128.

3,4,7,8-Tetrasilacycloocta-1,5-diyne, 3,6,7-Trisilacyclohepta-1,4-diyne, and Related Compounds. New Class of Cyclic Compounds Composed of Polysilanes and Acetylenes[1]

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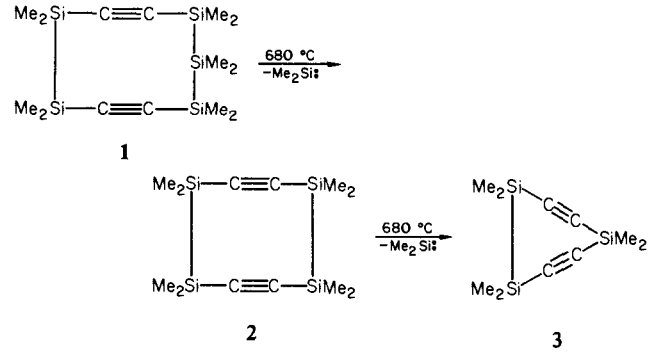
Although several types of cyclic polysilanes having carbon–carbon multiple bonds in the ring are known,[2] no cyclic ethynylene polysilane has been reported. As shown in a qualitative molecular orbital diagram of 3,4,7,8-tetrasilacycloocta-1,5-diyne in Figure 1, two Si–Si σ orbitals can overlap with one of two π orbitals[3,4] of each C≡C bond to make up new molecular orbitals with through-conjugation. Therefore, it is extremely intriguing to examine the properties of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**1**), if it can be prepared. On the other hand, neither spatial nor through-bond interaction between two acetylenes has been observed for the corresponding cycloocta-1,5-diyne, the smallest known cyclic diyne.[5]

We have adopted a ring-contraction method[6] for the preparation of **1** (Scheme I). Irradiation with a low-pressure mercury lamp[6] or flash vacuum pyrolysis (FVP, 650 °C (10^{-2}–10^{-3} mmHg)) of **2**, prepared in 37% yield by the reaction of a di-Grignard reagent from 1,2-diethynyl-1,1,2,2-tetramethyldisilane with 1,3-dichlorohexamethyltrisilane, resulted in the formation of **1** as a crystal in 10% and 63% yield, respectively, with concomitant extrusion of dimethylsilylene, which was trapped with diethylsilane. Poorer yield in the photochemical process than in FVP may be ascribed to the fact that the product (**1**) has stronger absorption than the precursor in the 240–260-nm region, as shown later.

Surprisingly, from the pyrolysis products, 3,3,6,6,7,7-hexamethyl-3,6,7-trisilacyclohepta-1,4-diyne (**3**) was isolated as a white crystal in 3% yield. Apparently, **1** is the direct precursor to **3**, as evidenced by the fact that the FVP of **1** (680 °C (10^{-2}–10^{-3} mmHg)) gave **3** in 6.3% yield.

As far as we know, **3** is the smallest known cyclic diyne. Although unstable in air, **3** can be purified by sublimation to give correct analyses. Several interesting features can be pointed out from Table I, which lists physical properties of ethynylene polysilanes, but the most striking fact is an enhanced bathochromic

Scheme I



(1) Chemistry of Organosilicon Compounds. 167.
(2) Inter alia (a) Disilacyclobutanes: Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43. (b) Disilacyclohexadienes: Nakadaira, Y.; Kanouchi, S.; Sakurai, H. *J. Am. Chem. Soc.* **1974**,, *96*, 5623.
(3) For a review: Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.
(4) Ensslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.* **1974**, *96*, 2757 and references therein.
(5) Koster-Jensen, E.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 671.
(6) (a) Sakurai, H.; Kobayashi, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1971**, *93*, 5272; (b) **1974**, *96*, 2656.

0002-7863/83/1505-3359$01.50/0