Reaction of a Highly Spiro-activated Electrophilic Cyclopropane with Pyridines; an Unusual Solvent Effect on Reaction Rate

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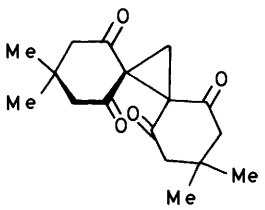
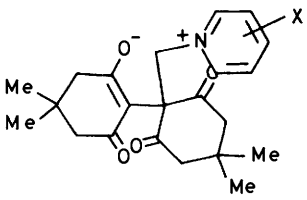
The kinetics of the reaction of 3,3,10,10-tetramethyldispiro[5.0.5.1]tridecane-1,5,8,12-tetraone (**1**) with pyridine was studied in various pure solvents (protic and aprotic). Although this reaction afforded a polar zwitterion [the pyridinium β-oxoenolate derivative (**2**)], the solvent effect on the reaction rate was not as remarkable as that in the Menschutkin reaction; it was related to Gutmann's *DN* parameters rather than to the Dimroth–Reichardt E_T values. The multiparameter analysis approach according to the Krygowski–Fawcett model in aprotic solvents and the Taft–Kamlet model in protic solvents was successful, giving log $k_2 = -8.82 \times 10^{-3}E_T - 17.4 \times 10^{-3}DN - 3.36$ ($r = 0.927$; $n = 8$) and log $k_2 = -0.734\alpha + 0.162\beta - 3.15$ ($r = 0.941$; $n = 6$), respectively. Mechanisms are discussed.

The influence of solvents on the rates of chemical reactions has been investigated extensively. Many attempts have been made to explain kinetic effects of the medium in terms of physical or thermodynamic properties of the solution.[1-3] The Menschutkin reaction has long been regarded as one of the most extreme examples of solvent effects on reaction rate. In this reaction, since ammonium halides are formed from neutral substrates, large increases in rate have been observed with increased polarity of the solvent.[2] Generally, such a reaction, which affords ionic products from neutral materials, is accelerated in polar solvents.[1b,3]

We have previously reported the preparation of 3,3,10,10-tetramethyldispiro[5.0.5.1]tridecane-1,5,8,12-tetraone (**1**) and the ready formation of a zwitterion, the pyridinium β-oxoenolate (**2**), in its reaction with pyridines.[4] Although this reaction furnished polar products (**2a–c**) under mild conditions, rate depression rather than acceleration was observed in polar aprotic solvents, in comparison with a non-polar solvent such as benzene.[4d] Here we discuss this unusual solvent effect in detail, on the basis of multiparameter analysis.



(**1**)



(**2**) **a**; X = H
b; X = 4-Me
c; X = 2-Me

Results and Discussion

Kinetic Data for the Reaction of (**1**) *with Pyridines in Various Solvents.*—The reaction of (**1**) with pyridines gave rise to (**2a—c**) in quantitative yield (as estimated spectrometrically) in various solvents even at room temperature.[4] The kinetics of the reaction of (**1**) with pyridine (0.1M) were studied at several temperatures in various solvents with the pyridine in large stoicheiometric excess. The kinetics of the reaction were monitored at the charge-transfer band of (**2a**). The second-order rate constants (k_2) were determined by a previously described method.[4d] The values and thermodynamic parameters are summarized in Table 1, in which the related solvent parameters are also listed. The solvent effect on reactivity with α- and γ-picoline was investigated by the same methodology (Table 2).

At first glance, the solvent effect seems peculiar in comparison with the usual effect in the formation of ammonium salts from neutral molecules such as the Menschutkin reaction. The reaction in benzene solution proceeded more smoothly than that in more polar aprotic solvents such as dimethyl sulphoxide, dimethylformamide, *etc.*[4d] Furthermore, the (**1**)–pyridine reaction is decelerated by a factor of 0.33 in acetonitrile solution as compared with that in benzene, whereas most Menschutkin reactions or ionic [2 + 2] cycloadditions are accelerated in acetonitrile, as shown in Table 3.

A general theory describing solvent effects on physicochemical properties measured in solution has not been developed to date. However, in many cases, reliable predictions can be obtained from empirical relationships.[1,5] Recently, Krygowski and Fawcett, and Taft and Kamlet have reported models of multiparameter analysis for solvent effects.[6,7] The application of the former model is not possible for all solvents, because *DN*-values are not available for most protic solvents. We will treat medium effects in aprotic and protic solvents separately.

Solvent Effects in Aprotic Media.—In the reaction of (**1**) with pyridine, correlation with Gutmann's *DN* values[8] was fair for the aprotic solvent series (log $k_2 = -1.80 \times 10^{-2}$ *DN* − 3.72; $r = 0.902$, $n = 8$); no correlation between log k_2 and the Dimroth–Reichardt E_T values was observed.[9] In the Krygowski and Fawcett model,[6] it was postulated that the solvent effect on a physicochemical quantity could be represented as a linear function of two independent but complementary parameters describing the Lewis acidity and Lewis basicity of the given solvent. In this case, the Dimroth–Reichardt E_T value is chosen as a measure of Lewis acidity, and Gutmann's *DN* value is used as a measure of solvent basicity. Although the E_T parameter is often assumed to be associated with electrostatic solvation, Krygowski and Fawcett have proposed that the parameter is a quantitative measure of the Lewis acidity of the solvent. Similar conclusions have been reached by Koppel and Palm.[1a] Recently, Swain *et al.* have suggested that E_T represents parameters that are more sensitive to *A*, an anion-solvating tendency ('acity'), than to *B*, a cation-solvating tendency ('basity'), whereas Gutmann's donor number *DN* might be expected to approximate to *B*.[5c] According to the foregoing model, the logarithm of the rate constant (log *k*) can be

Table 1. Kinetic data for the reaction of (**1**) with pyridine

(a) Aprotic solvents

Solvent[a]			Temp.	Rate const.	Activation parameters[e]	
E_T[b]	DN[c]	ε[d]	(°C)	$10^{-5}\ k_2$/dm^3 mol^{-1} s^{-1}	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal K^{-1} mol^{-1}
Benzene			41.7	86.6		
			35.0	49.7		
34.5	0.1	2.3	25.0	24.4	13.3	−30.5
			17.1	12.9		
$(CH_2Cl)_2$			41.7	64.6		
			35.0	41.3		
41.9	0	10.37	25.0	17.0	15.1	−25.0
			17.1	7.77		
1,4-Dioxane			41.7	53.5		
			35.0	35.1		
36.0	14.8	2.2	25.0	13.6	14.4	−27.9
			17.1	7.41		
Acetonitrile			41.7	29.2		
			35.0	20.5		
46.6	14.1	37.5	25.0	8.00	14.8	−27.6
			17.1	3.79		
THF			41.7	38.6		
			35.0	24.5		
37.4	20.0	7.4	25.0	7.80	16.8	−20.8
			17.1	3.95		
EtOAc			41.7	28.8		
			35.0	16.8		
38.1	17.1	6.0	25.0	7.56	14.5	−28.7
			17.1	3.06		
Me_2SO			41.7	29.7		
			35.0	16.7		
45.0	29.8	48.9	25.0	6.76	14.6	−28.5
			17.1	3.88		
Me_2NCHO			41.7	21.9		
			35.0	12.7		
43.8	26.6	36.7	25.0	6.20	14.4	−29.6
			17.1	2.76		

[a] THF = tetrahydrofuran. [b] Ref. 9. [c] Ref. 8. [d] Dielectric constant. [e] Activation parameters were evaluated from the plot of ln k_2 *vs.* $1/T$; correlation coefficients were more than 0.990.

(b) Protic solvents

Solvent[a]			Temp.	Rate const.	Activation parameters[c]	
α[a]	β[a]	ε[b]	(°C)	$10^{-5}\ k_2$/dm^3 mol^{-1} s^{-1}	$\Delta H^{\neq}$/kcal mol^{-1}	$\Delta S^{\neq}$/cal K^{-1} mol^{-1}
MeOH			41.7	83.1		
			35.0	46.2		
0.990	0.615	32.6	25.0	16.0	16.1	−21.6
			17.1	9.07		
EtOH			41.7	90.7		
			35.0	54.9		
0.850	0.773	24.3	25.0	21.3	14.6	−26.3
			17.1	12.1		
Pr^iOH			41.7	102		
			35.0	79.7		
0.687	0.949	18.3	25.0	29.2	12.2	−33.4
			17.1	19.9		
Bu^nOH			41.7	165		
			35.0	86.0		
0.710	0.884	17.1	25.0	38.2	14.8	−24.5
			17.1	20.1		
Bu^tOH			41.7	133		
			35.0	80.3		
0.436	1.014	12.2	25.0	45.8	11.2	−36.1
$PhCH_2OH$			41.7	156		
			35.0	82.7		
0.430	0.498	13.1	25.0	41.8	13.0	−30.2
			17.1	23.6		

[a] Ref. 7. [b] Dielectric constant. [c] Activation parameters were evaluated from the plot of ln k_2 *vs.* $1/T$; correlation coefficients were more than 0.990.

Table 2. Kinetic data for the reactions of (**1**) with 2-methylpyridine and 4-methylpyridine in various solvents at 25.0 °C

Solvent	Rate const. 10^{-5} k_2/dm^3 mol^{-1} s^{-1}
	2-Methylpyridine
Benzene	1.24
$(CH_2Cl)_2$	1.11
1,4-Dioxane	0.95
MeCN	0.79
THF	0.79
EtOAc	0.76
Me_2SO	0.74
Me_2NCHO	0.70
	4-Methylpyridine
Benzene	40.3
$(CH_2Cl)_2$	32.2
1,4-Dioxane	29.3
MeCN	16.0
THF	12.9
EtOAc	12.3
Me_2SO	12.3
Me_2NCHO	10.0
EtOH	34.2

[a] THF = tetrahydrofuran.

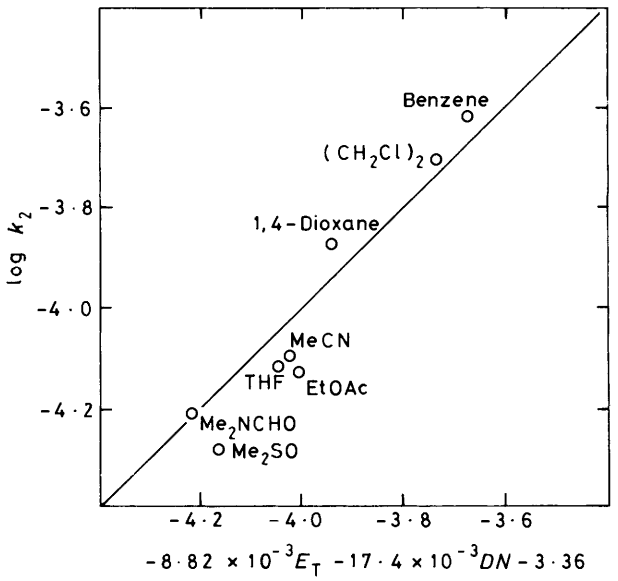


Figure 1. Observed *vs.* calculated rate constants for the reaction of (**1**) with pyridine at 25.0 °C

described in terms of equation (1), where a and b are constants describing the sensitivity of log k to acidic and basic solvent properties.[6b]

$$\log k = aE_T + bDN + c \quad (1)$$

This two-parameter equation is now applied to the reaction of (**1**) with pyridines and some of the related Menschutkin reactions. The results are summarized in Table 4 and illustrated in Figure 1. Good linearity is observed for the solvent effect of the present reaction in aprotic solvents. The regression coefficients (a, b, c) were calculated by the least-squares method, yielding equation (2).

$$\log k_2 = -8.82 \times 10^{-3}E_T - 17.4 \times 10^{-3}DN - 3.36 \quad (2)$$

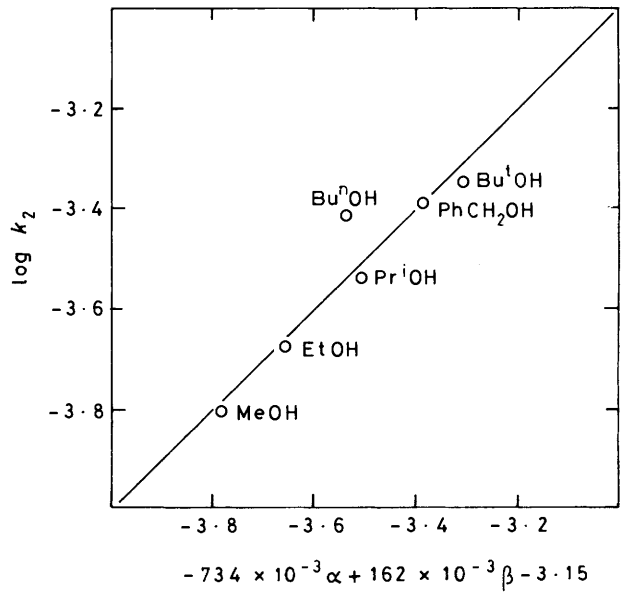


Figure 2. Observed *vs.* calculated rate constants for the reaction of (**1**) with pyridine at 25.0 °C

The kinetic solvent effects in the Menschutkin reactions generally depend more on the E_T value of a solvent than on *DN*; the larger the E_T value, the greater the reactivity. This phenomenon has been explained in terms of solvation of the charge-separated transition state at the rate-determining step.[1b,3] In contrast, *DN* rather than E_T of a solvent influences the reactivity of (**1**) with pyridines. Thus, the smaller *DN*, the greater the reactivity in these reactions. The negative coefficient of *DN* suggests that nucleophilic solvation towards (**1**) might depress its reactivity with pyridines. Furthermore, the coefficient (a) of E_T is negative and the contribution (18%) of solvent acidity to the solvent effect is small, whereas Menschutkin reactions show positive coefficients for E_T and large contributions.[1b]

Solvent Effects in Protic Media.—The analysis of solvent effect for protic media was carried out by using the Taft–Kamlet equation (3),[7] involving the solvent hydrogen-bond donor ability (HBD) (α-scale) and acceptor ability (HBA) (β-scale), where a and b represent the sensitivities of log k to α and β. The results and related data are collected in Table 5 and illustrated in Figure 2. The regression coefficients were calculated similarly [equation (4)].

$$\log k = a\alpha + b\beta + c \quad (3)$$

$$\log k_2 = -0.734\alpha + 0.162\beta - 3.15 \quad (4)$$

The present reaction depends more on the α-scale, and becomes slower with larger α-values in protic solvents. This decrease in reactivity might be attributable to deactivation of the nucleophile (pyridine) by hydrogen bonding with the protic solvent.[10]

In Menschutkin reactions, the contribution of HBA to the solvent effect is larger than that of HBD, and the signs of both coefficients are negative. Thus, the larger the β-value of a medium, the lower the reactivity. Generally, a specific inhibitory effect and a specific catalytic effect compete in the influence of protic solvents. Indeed, the reaction of β-phenethyl halides with 1,4-diazabicyclo[2.2.2]octane was affected by formation of a hydrogen-bonded complex between a protic solvent and the

Table 3. Relative rates (polar *vs.* nonpolar solvent)

Reaction	(1) + pyridine	(1) + α-picoline	$BrCH_2CO_2Et$ + Et_3N	$PhCH_2CH_2Cl$ + DABCO	$NO_2C_6H_4CH_2Cl$ + Me_3N	$(CN)_2C{=}C(CN)_2$ + MeCH=CHOMe
k(MeCN)/k(C_6H_6)	0.33	0.64	27	53	170	496[a]
T/°C	25.0	25.0	20	54.5	20	30
Ref.	*b*	*b*	*c*	*d*	*e*	*f*

[a] k(MeCN)/k(CCl_4). [b] Present study. [c] (*a*) H. U. Halbau, *Z. Phys. Chem.*, 1913, **84**, 129; (*b*) M. H. Abraham, *J. Chem. Soc. B*, 1971, 299. [d] Ref. 2*e*. [e] Y. Drougard and D. Decroocq, *Bull. Soc. Chim. Fr.*, 1969, 2972. [f] G. Steiner and R. Huisgen, *Tetrahedron Lett.*, 1973, 3769.

Table 4. Krygowski–Fawcett description of solvent effects on the rate of reaction of (1) with pyridines and some Menschutkin reactions

$$\log k_2 = aE_T + bDN + c$$

Reaction	10^{-3} a	10^{-3} b	c	ā(%)[a]	b̄(%)[a]	Corr. coefft.	*n*	Ref.
(1) + pyridine	−8.82	−17.4	−3.36	18	82	0.927	8	*b*
(1) + α-picoline	−3.60	−6.92	−4.81	17	83	0.930	8	*b*
(1) + γ-picoline	−8.66	−17.1	−3.13	17	83	0.891	8	*b*
MeI + pyridine	1.71	0.09	−8.74	92	8	0.996	6	*c*
$PhCH_2CH_2I$ + DABCO	154	2.16	−6.69	97	3	0.936	9	*d*
$ClCH_2CO_2Et$ + Et_3N	144	−20.7	−6.72	79	21	0.974	5	*e*
$PhCOCH_2Br$ + $PhNH_2$	85.6	0.77	−7.54	99	1	0.937	6	*f*

[a] % contribution.[6] [b] Present study. [c] N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1936, 1353. [d] Ref. 2*e*. [e] Ref. *c*, Table 3. [f] Ref. 13.

Table 5. Taft–Kamlet description of solvent effects on the rate of reaction of (1) with pyridine and some Menschutkin reactions

$$\log k_2 = a\alpha + b\beta + c$$

Reaction	10^{-3} a	10^{-3} b	c	ā(%)[a]	b̄(%)[a]	Corr. coefft.	*n*	Ref.
(1) + pyridine	−734	162	−3.15	83	17	0.941	6	*b*
$PhCH_2CH_2I$ + DABCO	−54.1	−753	−0.753	7	93	0.945	6	*c*
Ph_2CH_2Br + DABCO	−82.2	−598	−1.42	11	89	0.956	6	*c*
$PhCH_2CH_2Cl$ + DABCO	−176	−615	−3.02	24	76	0.936	6	*c*

[a] % contribution.[6] [b] Present study. [c] Ref. 2*e*.

amine or the halide.[2e] Recently, Johnson *et al.* have pointed out the importance of hydrogen bonding between pyridine and methanol in quaternization of pyridine with ethyl iodide.[11]

Notwithstanding, (1) reacted more smoothly with pyridine in protic solvents than in dipolar aprotic solvents, despite the fact that the Menschutkin reaction is generally decelerated in protic solvents.[2e,12] These results indicate that hydrogen bonding in a protic medium not only deactivates the nucleophile (pyridine) but also considerably activates (1). A similar tendency has been observed in the solvent effect on the reaction of phenacyl bromide with aniline.[13]

In addition to this effect, the sign of the coefficient for β has been found to be positive, although its contribution is much less than the hydrogen-bond donor ability. The hydrogen-bond accepting ability would slightly assist the formation of a pyridinium cation in the reaction of (1) with pyridine. The result is also contrary to observations on the Menschutkin reaction.

Thermodynamic Properties of the Reaction of (1) *with Pyridine.*—The dependence on temperature of the second-order rate constants for the reaction of (1) with pyridines gives values of the activation enthalpy and entropy as shown in Tables 1 and 2.

It is considered that the greater activation free energy in polar aprotic solvents, *e.g.* Me_2NCHO or Me_2SO, than in benzene is due to a larger activation enthalpy. The principal cause of increased activation enthalpy in a dipolar aprotic solvent might be increased solvation of reactant, *e.g.* (1), in the initial state. A similar phenomenon has been observed in some Diels–Alder reactions.[14]

In protic solvents, the greater the degree of HBD of solvent,

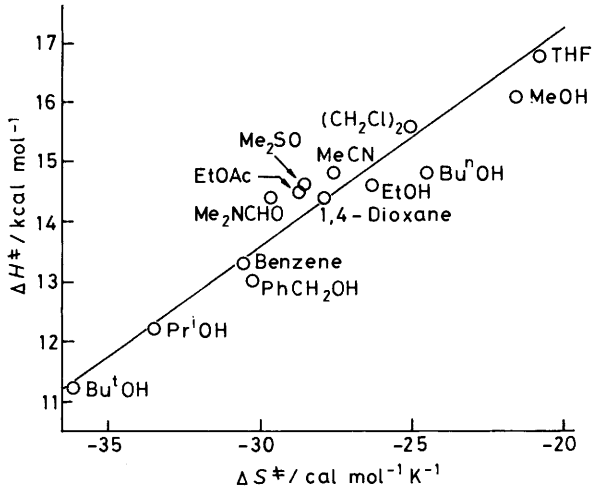


Figure 3. Isokinetic relationship for the solvent effect of the reaction of TACP with pyridine at 25.0 °C. $\Delta H^{\ddagger} = 0.335, \Delta S^{\ddagger} + 23.6$ ($r = 0.960$; $n = 14$)

the larger the activation enthalpy and the less negative the activation entropy. These kinetic parameters can be explained on the assumption that protic solvents stabilize the nucleophile, pyridine in the present case, rather than activate (1) in the ground state by hydrogen solvation.

As shown in Figure 3, the isokinetic relationship can be realized for all the solvents.[15] This result suggests that

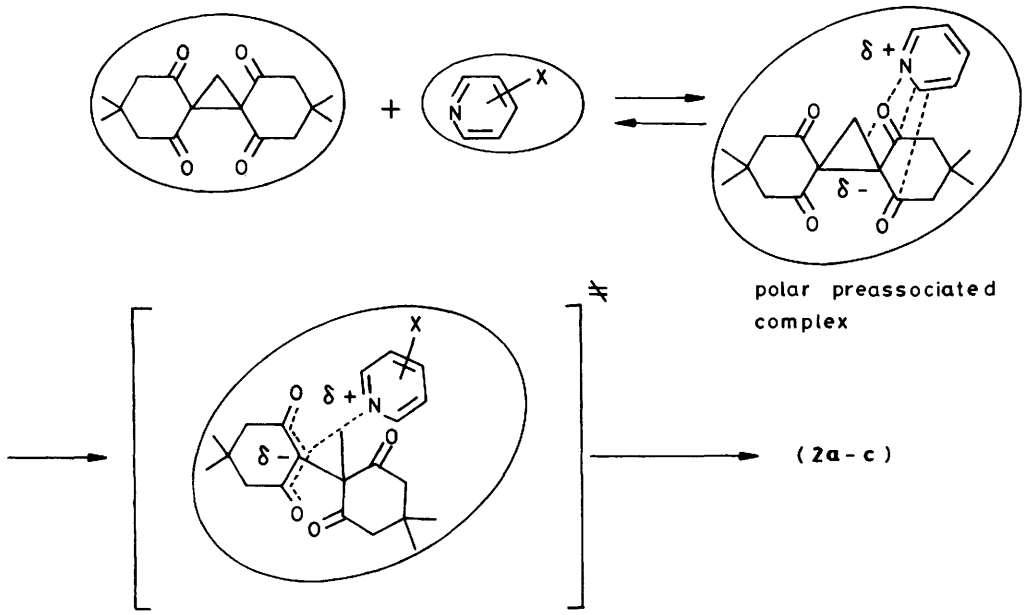


Figure 4. Preassociation mechanism in the reaction of (**1**)

mechanistic aspects of the reaction of (**1**) with pyridine in one solvent are not drastically different from those in any other solvent.

Mechanistic Considerations.—We now discuss solvent effects on kinetic processes as approached from the viewpoint of multiparameter analyses. This approach, which is informative concerning solvation in a ground or a transition state, may enable one to deduce subtle effects in a reaction. On the basis of the results, one can consider two possible explanations for the unusual solvent effect in the reaction of (**1**) with pyridine.

First, we can assume a bimolecular mechanism involving pre-equilibration (Figure 4).[4d,16] In this mechanism (**1**) reacts with pyridine to form a polar encounter complex prior to the rate-determining step (although the complex was neither isolated nor detected by spectroscopy).[17] The polar encounter complex might be regarded as a charge-transfer complex. The formation of such a complex is favoured in non-polar solvents.[18]

Alternatively, the solvent effect may result from the following two factors. (i) A highly spiro-activated electrophile such as (**1**) is so strongly solvated, especially by a powerful nucleophilic solvent, that its reactivity would tend to decrease. The other reactant, pyridine, is also solvated by a solvent which possesses higher HBD ability. The reactivity of the nucleophile would tend to decrease similarly. (ii) It has been suggested that in the highly reactive bimolecular systems the transition state is similar in structure to the initial state (a 'reactant-like' or 'early' transition state), and that there is little charge development in the transition state; such a situation mainly reflects a reactive electrophile (Figure 5). In this case specific solvation of the reactants (destroyed as one moves to the transition state) is the dominant factor.

In conclusion, though the reactions of (**1**) with pyridine are formally analogous to the Menschutkin reaction with respect to the formation of ionic products from neutral dipolar molecules, the solvent effects on rates are very different. Multiparameter analysis and thermodynamic considerations in the present reaction suggest that pre-equilibration or solvation of the starting materials may be very important influences on the reactivity of a highly spiro-activated electrophilic cyclopropane such as (**1**).

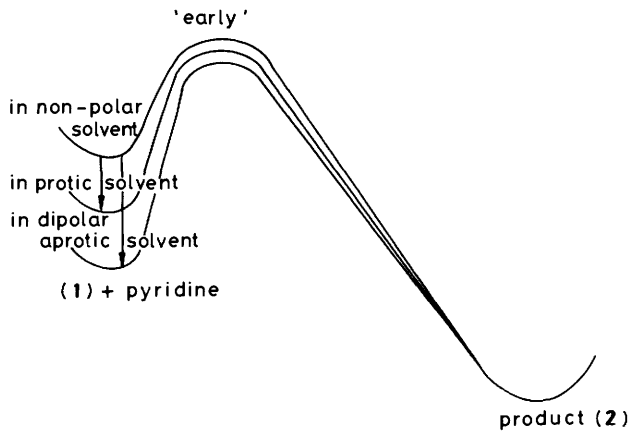


Figure 5. 'Reactant-like' or 'early' transition state in the reaction of (**1**)

Experimental

Materials.—3,3,10,10-tetramethyldispiro[5.0.5.1]tridecane-1,5,8,12-tetraone (**1**) was prepared by the method described earlier.[4b] Pyridines were purified by distillation after being described over potassium hydroxide.

Purification of Solvents.—Ethyl acetate was distilled over phosphorus pentaoxide. The other solvents were purified by the method described earlier.[4c]

Kinetic Measurements.[4d]—A Hitachi 124 spectrometer with thermostatted cell block was used for all absorption measurements. A stock solution of (**1**) (0.01M) was prepared by dissolving a carefully weighed amount in purified solvent. A stock solution of pyridine (1.00M) was prepared by the same method. A measured volume (1.00 ml) of the pyridine solution was placed in a 10 ml volumetric flask which was subsequently made up with the same solvent [(**1**)/pyridine 0.001M/0.1M]. The desired amount of the solution (*ca.* 4 ml) was placed in a 1 cm stoppered cell and the cell was immersed in a constant-temperature bath (±0.03 °C). After an appropriate time (*ca.* 30

min, at which point an accurate timer was started) the initial absorbance (A_0) of the solution at an appropriate wavelength (390 nm) in the charge-transfer band was measured. The reaction was followed by monitoring the increase in the absorbance (A) with time at the same wavelength. The final absorbance (A_∞) was determined after *ca.* 10 half-lives. The rate constant for the reaction was evaluated from a plot of ln $[(A_\infty - A_0)/(A_\infty - A)]$ *vs.* time.

In all cases the reaction was followed to *ca.* 80% completion. Two different techniques were used to measure the rate of the same reaction. The results are summarized in Tables 1 and 2.

Product Analysis.—To a solution of (**1**) (500 mg, 1.7 mmol) in benzene (30 ml) was added α-picoline (0.5 ml, 5.1 mmol) at room temperature, and the mixture was stirred for 1 week at the same temperature. After the removal of solvent under reduced pressure at room temperature, the crystalline product was filtered off. Recrystallization from chloroform gave pure 2-[4,4-*dimethyl*-1-(2-*methylpyridiniomethyl*)-2,6-*dioxocyclohexyl*]-5,5-*dimethyl*-3-*oxocyclohex*-1-*enolate* (**2c**) (600 mg, 91%), m.p. 164—165 °C; $\nu_{max.}$(Nujol) 1 630, 1 680, and 1 710 cm^{-1}; δ_H ($CDCl_3$) 9.07 (d, *J* 7 Hz, 1 H), 8.10 (t, *J* 7 Hz, 1 H), 7.40—7.63 (m, 2 H), 5.29 (s, 2 H), 3.02 and 2.22 (ABq, *J* 12 and 4 Hz), 2.60 (s, 3 H), 1.88 (s, 2 H), 1.79 (s, 2 H), 1.10 (s, 3 H), 1.05 (s, 3 H), 0.85 (s, 3 H), and 0.80 (s, 3 H); $\lambda_{max.}$(CH_3CN) 375 (log ε 3.0) and 289 nm (4.1) (Found: C, 72.0; H, 7.7; N, 3.7. $C_{23}H_{29}NO_4$ requires C, 72.0; H, 7.6; N, 3.65%).

The other products (**2a** and **b**) were obtained by the same procedure.[4c]

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