Base-Catalyzed Reactions. XXXVII.[1] Relative Rates of Side-Chain Alkenylation of 4-Substituted Pyridines with Isoprene. Effects of the Side-Chain Double Bond on Reaction Rates

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The competitive side-chain alkenylation of various 4-alkyl and alkenylpyridines with isoprene catalyzed by alkali metals was investigated. Examination of the alkylpyridines used in the reaction shows that steric factors are important when substitution is made on the carbon β to the pyridine ring. The presence of a side-chain double bond increases the rate of alkenylation and this is ascribed to a complexation of the olefinic bond with the alkali metal catalyst. The relative increase in competitive rate varies with the catalyst used in the reaction, such that K > Na > Li. The changes in reactivity that occur when using different catalysts are explained by the principle of hard and soft acids and bases. A table identifying many new 4-substituted pyridine compounds is also given.

It was noted in the preceding paper[1b] that, when isoprene was added to 4-picoline, the diadducts were formed very rapidly, even though the monoadducts were in very small concentrations. Diaddition products became detectable when only *ca.* 2% of the 4-picoline had been converted into monoadducts. The same results were observed when butadiene was added to 4-picoline in a similar reaction.[3] The side-chain double bond in these cases increases the overall rate of addition of a second conjugated diene.

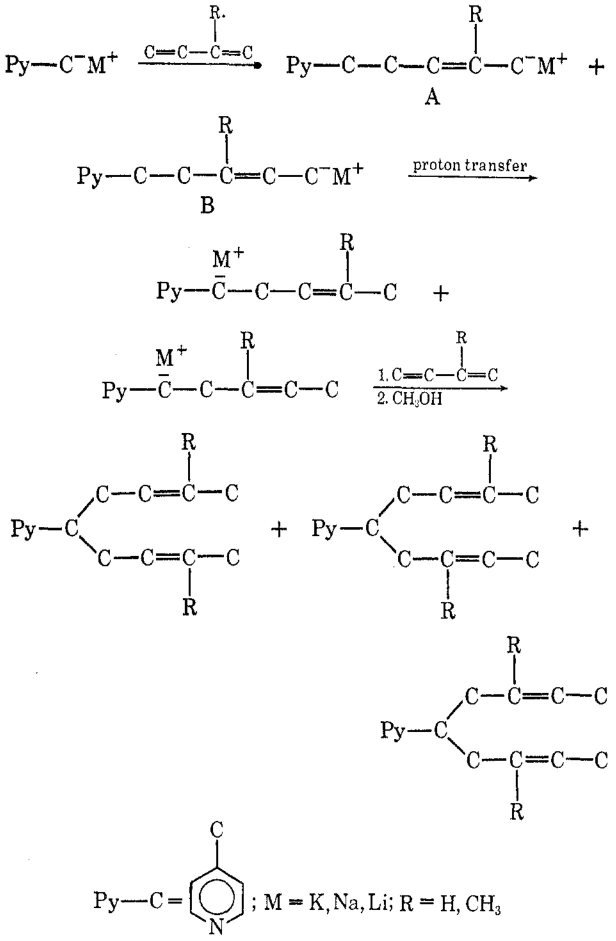
It was initially suggested[3] that this rate enhancement is due to a π-electron bonding of the picolyl[4] hydrogen with the double bond of the alkenyl group or aryl group, thus increasing the acidity of the alkenylated pyridines over that of the corresponding alkylpyridines. Similar increases in acidity of otherwise unactivated C–H bonds in camphenilone due to formation of homoenolate anions have also been noted.[5] Further studies now indicate that other factors may be of greater importance in the type of compounds presently being investigated. We now suggest that internal protonation of the anion formed by addition of a diolefin and complexation of the alkali metal with the side-chain double bond are the main contributors to the rate enhancement. Similar reports of the interaction of metals, such as lithium[6] and silver,[7] with olefinic bonds are known.

This study examines the reaction of isoprene at room temperature with various 4-alkyl- and alkenylpyridines. The steric effect of substitution is examined as well as the effect of changing the alkali metal catalyst.

Results and Discussion

The base-catalyzed alkenylation of 4-picoline with butadiene proceeds to only 1.5% completion before diaddition formation is noted.[3] When isoprene is added to 4-picoline, diaddition is found when the reaction has proceeded to about 2% completion.[1b] In these two cases the monoadducts react about 65 and 50 times faster, respectively, than does 4-picoline. Scheme I shows the general reaction of interest.

Scheme I



In order to determine the effect of structure on reaction rate, a large number of 4-substituted pyridines were synthesized. These compounds are listed in Table I, along with their physical constants. All new compounds were identified by nmr. Competitive reactions were then carried out using isoprene as the diolefin, with either 4-picoline or 4-*n*-propylpyridine in

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[1] (a) Paper VIII of the series Alkylation of Heteroaromatics. For paper VII and XXXVI of the series Base-Catalyzed Reactions, see ref 1b. (b) W. M. Stalick and H. Pines, *J. Org. Chem.*, **35**, 415 (1970).

[2] Monsanto Predoctoral Fellow, 1965–1966; Ethyl Corp. Predoctoral Fellow, 1967–1968.

[3] H. Pines and J. Oszczapowicz, *J. Org. Chem.*, **32**, 3183 (1967).

[4] Picolyl anion throughout the paper is defined as an anion on the α-carbon atom of the alkyl group on pyridine.

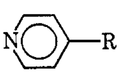
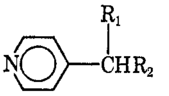
[5] (a) A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **88**, 1905 (1966); (b) A. Nickon, J. L. Lambert, and J. E. Oliver, *ibid.*, **88**, 2787 (1966).

[6] J. P. Oliver, J. B. Smart, and M. T. Emerson, *ibid.*, **88**, 4101 (1966).

[7] D. Gray, R. A. Wies, and W. D. Closson, *Tetrahedron Lett.*, 5639 (1968).

TABLE I

SYNTHESIS OF 4-SUBSTITUTED PYRIDINES

Starting Materials		Products					
							
R	Alkylating agent	R_1	R_2	Registry no.	Isolated yield, %	Bp,[a] °C (mm)	$n^{20}D$
C_2H_5	C_2H_5Br	CH_3	C_2H_5		98[b,c]	128–130 (100)	1.4958
CH_3	i-C_3H_7Br	H	i-C_3H_7		79[d]	81 (15)	1.4896
C_2H_5	i-C_3H_7Br	CH_3	i-C_3H_7		98[c,d]	89 (15)	1.4930
CH_3	i-$C_5H_{11}Br$	H	i-C_5H_{11}	22241-38-9	85[c]	77–79 (3.5)	1.4874
CH_3	$CH_3CH(C_2H_5)CH_2Br$	H	$CH_2CH(CH_3)C_2H_5$	22241-39-0	92	78 (2.5)	1.4907
CH_3	C_4H_9Br	H	C_4H_9		93[e]	62–65 (2)	1.4920
CH_3	C_3H_7Br	H	C_3H_7		94[f]	84 (10)	1.4939
CH_3	i-C_4H_9Br	H	i-C_4H_9	4810-78-0	78	70 (3)	1.4903
CH_3	$(CH_3)_3C(CH_2)_2Br$	H	$(CH_2)_2C(CH_3)_3$	22241-41-4	90	89–90 (4)	1.4920
CH_3	$C_5H_{11}Br$	H	C_5H_{11}		87[g]	86–88 (4)	1.4891
CH_3	$H_2C{=}CH(CH_2)_2Br$	H	$(CH_2)_2CH{=}CH_2$	22241-42-5	80	102 (13)	1.5087
CH_3	$H_2C{=}CH(CH_2)_3Br$	H	$(CH_2)_3CH{=}CH_2$	22241-43-6	86	85–86 (3)	1.5052
C_2H_5	i-$C_5H_{11}Br$	CH_3	i-C_5H_{11}	22253-33-4	61[c]	98–100 (8)	1.4869
C_2H_5	$CH_3CH(C_2H_5)CH_2Br$	CH_3	$CH_2CH(CH_3)C_2H_5$	22253-34-5	70[c]	98–99 (8)	1.4895

[a] Boiling points are uncorrected. [b] Literature bp 197° (765 mm), $n^{20}D$ 1.49515 [C. T. Kyte, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 4454 (1960)]. [c] Yield calculated by vpc. [d] Previously synthesized in this laboratory [H. Pines and B. Notari, *J. Amer. Chem. Soc.*, **82**, 2209 (1960)]. [e] Literature bp 95° (6 mm), $n^{20}D$ 1.49196 (cited in *b*). [f] Literature bp 84° (8 mm), $n^{20}D$ 1.49387 (cited in *b*). [g] Literature bp 68.5° (0.1 mm), $n^{20}D$ 1.4886 [J. P. Wibaut and J. W. Hey, *Rec. Trav. Chim. Pays-Bas*, **72**, 513 (1953)].

competition with the synthesized pyridine. *Ca.* 5 g-atom % of metallic sodium was dispersed in an equimolar amount of the two 4-substituted pyridines to form the catalyst, and then about 10 mol % of isoprene was added to this mixture. Samples were removed periodically and the ratio of products was determined by vpc analysis; these competitive results were then corrected for variations in relative thermal conductivity and are summarized in Table II. The effect of anion stability on reaction rate can be inferred by examinination of expt 1 and 2. The secondary anion appears to be the most reactive; 4-picoline reacts more slowly owing to the stability of the anion, and the tertiary anion, although expected to be the most reactive, is slower, presumably because steric factors decrease the rate of addition to isoprene. Although the relative concentrations as well as the relative reactivities of the reactant anions contribute to the observed results, it appears that anion reactivity and steric hindrance effects are of major importance in the case of alkylpyridines. This assumption is further strengthened by the results discussed in the section dealing with solvent effects (see below). These results are in agreement with previous studies on the competitive rates of reaction of substituted aromatic hydrocarbons[8] and of 2- and 4-alkylpyridines[9,10] with ethylene carried out in an autoclave at elevated temperatures.

The relative rate of pentenylation of 4-*n*-propylpyridine is slower than that of 4-ethylpyridine by a factor of 2.5 (expt 5), probably owing to the increased bulk of the side chain. Further lengthening of the chain has only a slight effect on the rate of reaction, *n*-propyl-, *n*-butyl-, *n*-pentyl-, and *n*-hexylpyridine all being 3.5–4 times more reactive than 4-picoline (expt 3 and 7–9). Likewise, substitution for a hydrogen by a methyl group on a carbon atom γ or δ to the pyridine ring has little effect on the rate of reaction (expt 10–13). However, when the methyl substitution is on the carbon atom β to the pyridine ring, the rate of reaction decreases sharply within each series of anions (expt 1, 4, and 15 for tertiary anions and 2, 3, and 14 for secondary anions).

The effect of the side-chain double bond on the rate of isoprene addition can also be seen in Table II (expt 16, 19, and 20). The double bond of 4-(3-pentenyl)-pyridine (the butadiene adduct, expt 16) increases the rate of reaction with isoprene by a factor of *ca.* 10 over that of 4-picoline, while the isoprene monoadducts (expt 19 and 20) show a rate increase of about 7.5. The effect of the position of the double bond was examined in the case of 4-(3-pentenyl)-, 4-(4-pentenyl)-, and 4-(5-hexenyl)pyridine (expt 16–18), and it was found that the effect of the unsaturation decreases as the double bond is moved from the γ to the δ to the ϵ position with respect to the pyridine ring, the relative rates decreasing from 10 to 7 to 4, respectively. Unsaturation in the ϵ position has almost no effect on the reaction rate (expt 9 *vs.* 18).

In addition to sodium and potassium, it was found that lithium metal is also a catalyst for these reactions.[11] Changing the metal catalyst from potassium to sodium to lithium changes the competitive rate of pentenylation of 2-methyl-5-(4-pyridyl)-2-pentene *vs.* 4-*n*-propylpyridine from 2.6 to 2.2 and 1.9, respectively (expt 23, 19, and 25). However, no change in competitive reaction rates is noted when different metals are used as catalysts for the addition of isoprene to the saturated analog, 4-methyl-1-(4-pyridyl)pentane *vs.* 4-*n*-propylpyridine (expt 21, 10, and 24). The above results can be explained by applying the principle of hard and soft acids and bases.[12] An olefin is a soft base and as such is expected to form a more stable complex with the softest acid, potassium ion, and the least stable complex with lithium ion, which is the hardest acid in

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(8) H. Pines and L. Schaap, *J. Amer. Chem. Soc.*, **80**, 3076 (1958).

(9) H. Pines and L. Schaap, *Advan. Catal.*, **12**, 117 (1960).

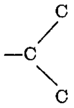
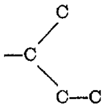
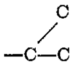
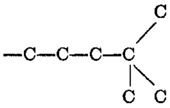
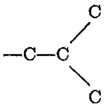
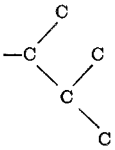
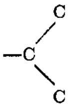
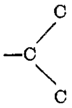
(10) B. Notari and H. Pines, *J. Amer. Chem. Soc.*, **82**, 2945 (1960).

(11) W. M. Stalick and H. Pines, *J. Org. Chem.*, in press.

(12) (a) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963); (b) R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

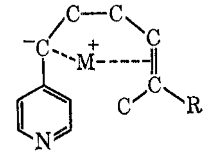
Table II

Competitive Pentenylation of 4-Substituted Pyridines[a]

Expt	4-Alkylpyridine 4-$C_5H_4NR_1$	 4-$C_5H_4NR_2$	Ratio of reacted $C_5H_4NR_1$/$C_5H_4NR_2$	Normalized ratio[b]
1		—C	2.0	2.0
2	—C—C	—C	8.2	8.2
3	—C—C—C	—C	3.4	3.4
4		—C	0.9	0.9
5	—C—C	—C—C—C	2.5	8.5
6		—C—C	0.24	2.0
7	—C—C—C—C	—C—C—C	1.2	4.1
8	—C—C—C—C—C	—C—C—C	1.1	3.7
9	—C—C—C—C—C—C	—C—C—C	1.0	3.4
10	$-C-C-C-\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	1.3	4.4
11	$-C-C-\overset{C}{\overset{\mid}{C}}-C-C$	—C—C—C	1.3	4.4
12	$-C-C-\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	1.3	4.4
13		—C—C—C	1.1	3.7
14		—C—C—C	0.05	0.2
15		—C—C—C	0	<0.01
16[c]	—C—C—C=C—C	—C—C—C	2.9	9.9
17	—C—C—C—C≡C	—C—C—C	2.1	7.1
18	—C—C—C—C—C=C	—C—C—C	1.3	4.4
19	$-C-C-C{=}\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	2.2	7.5
20	$-C-C-\overset{C}{\overset{\mid}{C}}{=}C-C$	—C—C—C	2.2	7.5
21[d]	$-C-C-C-\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	1.2	4.1
22[d]		—C—C	0.7	5.5
23[d]	$-C-C-C{=}\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	2.6	8.8
24[e]	$-C-C-C-\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	1.2	4.1
25[e]	$-C-C-C{=}\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	1.9	6.5
26[f]	$-C-C-C-\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	1.2	4.1
27[f]		—C—C	1.1	9.0
28[f]	$-C-C-C{=}\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	2.7	9.2
29[g]	$-C-C-C{=}\overset{C}{\overset{\mid}{C}}-C$	—C—C—C	2.7	9.2

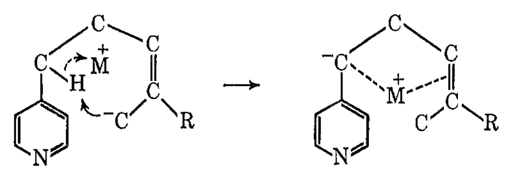
[a] Sodium metal was used as the catalyst initiator, unless otherwise noted. [b] Ratio of reacted $C_5H_4NR_1$/4-picoline normalized to 4-picoline = 1. [c] Mixture of *cis–trans* was used in ratio of 1:2. [d] Potassium metal was used as the catalyst initiator. [e] Lithium metal was used as the catalyst initiator. [f] Reaction was run in a homogeneous system using dimethyl sulfoxide as a solvent and potassium *t*-butoxide as a catalyst. [g] Reaction was run in a homogeneous system using N-methyl-2-pyrrolidone as a solvent and potassium *t*-butoxide as a catalyst.

this study. As a consequence, the stronger the metal-to-olefin complex, the larger the amount of negative charge on the picolyl carbon; the picolyl carbon thus becomes more nucleophilic and reacts more rapidly. The metal–double-bond complex is assumed to be a monomer, in analogy with the case of benzyllithium in tetrahydrofuran.[13] The rate increase that is realized



in this case is even more significant when one considers that the metal not only complexes with the side-chain double bond but is probably also stabilized intermolecularly by the lone-pair electrons of neighboring pyridine molecules.

The second factor which appears to play an important role in increasing the rate of addition is the internal protonation of the monoaddition product (A and B in Scheme I). Since a rate increase of 50 to 65 times is noticed in the case of the isoprene or butadiene monoadduct over that of 4-picoline, and 7.5 and 10 are the respective rate increases due to double-bond complexation of the metal, the other factor of 6.5 is probably due to the intramolecular protonation of the side chain and subsequent metalation of the picolyl carbon. The following diagram illustrates the assumed cyclic structure containing five carbon atoms and a bridging hydrogen; examination of space-filling molecular models shows this to be a favorable situation.



This mechanism implies that the product formed from internal protonation must be of a *cis* conformation about the double bond. If an examination is made of

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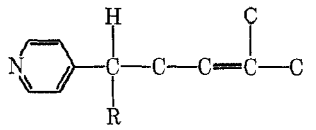
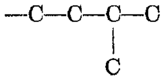
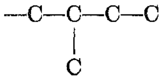
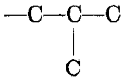
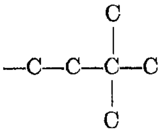
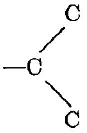
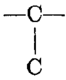
(13) P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

TABLE III

CHARACTERIZATION OF NEW PRODUCTS FORMED DURING COMPETITIVE STUDIES[a]



Products from expt no.[b]	R[c]	Registry no.	n^{20}_D	Calcd, %		Found, %	
				C	H	C	H
7	—C—C—C	22241-44-7	1.5042	82.70	10.41	82.52	10.35
8	—C—C—C—C	22241-45-8	1.5020	82.89	10.66	83.06	10.60
9	—C—C—C—C—C	22241-46-9	1.4996	83.05	10.89	82.84	10.78
10	 $-C-C-\underset{\displaystyle C}{\underset{\vert}{C}}-C$	22241-47-0	1.4990	83.05	10.89	83.06	10.78
11	 $-C-\underset{\displaystyle C}{\underset{\vert}{C}}-C-C$	22241-48-1	1.4998	83.05	10.89	82.72	10.78
12	 $-C-\underset{\displaystyle C}{\underset{\vert}{C}}-C$	22241-49-2	1.5002	82.89	10.66	82.57	10.49
13	 $-C-C-\overset{\displaystyle C}{\overset{\vert}{\underset{\displaystyle C}{\underset{\vert}{C}}}}-C$	22241-50-5	1.4960	83.20	11.09	83.47	10.99
14	 $-C\genfrac{}{}{0pt}{}{\diagup C}{\diagdown C}$	22241-51-6	1.5082	82.70	10.41	82.64	10.26
15	 $-\underset{\displaystyle C}{\underset{\vert}{C}}-C^{d}$	12241-52-7	1.5149	82.89	10.66	83.09	10.68
16	C—C=C—C *trans*	22256-21-9	1.5148	83.66	9.83	83.76	9.63
16	C—C=C—C *cis*	22256-22-0	1.5178	83.66	9.83	83.60	9.92
17	—C—C—C=C	22241-53-8	1.5126	83.66	9.83	83.69	9.71
18	—C—C—C—C=C	22241-54-9	1.5102	83.78	10.11	83.52	10.06

[a] The physical constants of all products of the competitive reactions not given here are given in Table IV of the preceding paper (see ref 1b). [b] Experiment numbers refer to those given in Table II. [c] The isoprene adduct shown is the one formed by C-4 addition of isoprene. Nmr studies indicate that the product isolated contains about 60–70% C-4 and 30–40% C-1 addition products; therefore, the elemental analyses and refractive indices given here are for the mixture. [d] This product is made from 4-(2-isoamyl)pyridine, so that the hydrogen represented in the main structure in this case is replaced by a methyl group.

the diaddition products of butadiene to 4-picoline, a ratio of 3.1:3.3:1.0 is found for the distribution of *trans,trans*/*trans,cis*/*cis,cis*. Indeed, the ratio of product containing a *cis*-butene group is much larger than the thermodynamically predicted ratio.[14,15]

Solvent Effects.—Similar catalytic reactions occur in homogeneous media of dipolar aprotic solvents using potassium *t*-butoxide as a catalyst.[16] To determine the effect of solvent on the competitive rates of reaction, four experiments were performed using dimethyl sulfoxide or N-methyl-2-pyrrolidone as solvents (Table II, expt 26–29). It was found that the effect of solvent on the competitive rates is small. This result is not too surprising, for although the reactions in the presence of the alkali metal catalyst have been made without added solvent, they are, in actuality, in a similar polar medium of excess alkylpyridine. This type of reaction has been tried in less polar solvents, such as tetrahydrofuran and dimethoxyethane, but no evidence for reaction was found.[17]

The competitive rate of alkenylation of 4-isopropylpyridine increased upon changing the catalyst from sodium to potassium to potassium *t*-butoxide; the competitive ratio of 4-isopropylpyridine/4-ethylpyridine changes from 0.24:1 to 0.7:1 to 1.1:1, respectively, so that, in the homogeneous system, 4-isopropylpyridine is more reactive than 4-ethylpyridine, as would be predicted by anion reactivity. It appears that the relative rate of pentenylation of 4-isopropylpyridine increases as the anion becomes more loosely associated with the alkali metal; and finally, in the dipolar aprotic solvents, the cation is solvated and the anion of 4-isopropylpyridine adds to isoprene faster than does the anion of 4-ethylpyridine. This factor is important, because there should be little if any steric hindrance to addition by 4-ethylpyridine; but 4-isopropylpyridine should experience steric hindrance to addition if the ion pair is closely related. In the preceding paper[1b] it was also shown that the amount of head-addition product becomes larger as the catalyst is changed from sodium to

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[14] The thermodynamic *cis*/*trans* ratio of 2-butenes at 27° was calculated to be about 1:3 (see ref 15). From this the calculated values expected for the diaddition product would be 9:6:1 for *trans,trans*/*trans,cis*/*cis,cis*.

[15] J. R. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **A36**, 559 (1946).

[16] H. Pines and W. M. Stalick, *Tetrahedron Lett.*, 3723 (1968).

[17] Unreported results from this laboratory.

potassium, which is in line with the increase in reactivity. Further substantiation of this point can be made by the fact that even with a sodium catalyst, the addition of these two alkylpyridines to ethylene was found to occur at the same rate when the reaction was run at elevated temperatures in an autoclave.[10]

Experimental Section

Synthesis of 4-Alkyl- and Alkenylpyridines.—The 4-substituted pyridines were prepared in liquid ammonia from 4-alkylpyridines, alkyl- or alkenylbromides, and sodium amide according to the general procedure described by Brown and Murphey.[18] Table I lists the products synthesized by this method along with their yields and physical constants.

Competitive Reactions.—The competitive reactions were carried out using the 4-substituted pyridines that had been dried over Linde 5-A Molecular Sieves and immediately redistilled before use. All materials were of >99.5% purity as determined by vpc. The following describes a typical competitive reaction: In a dry box, 0.025 mol of two 4-alkylpyridines were weighed and the alkylpyridines were then transferred to a three-necked flask of 20-ml capacity that had previously been flushed with nitrogen. The flask was equipped with a specially designed drum-shaped high-speed stirrer and a Dry Ice condenser to which a calcium chloride drying tube was attached. *Ca.* 2.5×10^{-3} g-atom of alkali metal was freshly cut and allowed to disperse in the combined alkylpyridines. After the metal was completely dispersed (2–3 hr), 5×10^{-3} mol of freshly distilled isoprene was added. Samples were withdrawn at 0.5-hr intervals for a total of 4 hr and decomposed with methanol. The products were then analyzed by vpc and the ratio of products was determined to calculate the relative rates of reaction. All products were synthesized individually and their physical constants and thermal conductivities were determined. All new products were identified by their nmr, ir, refractive indices, and elemental analyses. The new products are reported in Table III.

Homogeneous Catalyzed Reactions.—All of the needed reactants and solvents were distilled immediately before use. In a dry box, 0.025 mol of two 4-alkylpyridines were weighed and injected into a 30-dram vial containing 15 ml of a 0.5 *M* potassium *t*-butoxide in dimethyl sulfoxide or N-methyl-2-pyrrolidone solution. A rubber septum was inserted and the catalyst solutions were removed to the laboratory, where the reactions were carried out at room temperature following a procedure similar to that of Schriesheim and coworkers for the isomerization of olefins.[19] The samples from these reactions were quenched with methanol and the product ratios were determined by gas chromatography.

Analyses.—The infrared spectra of the pyridines were taken with a Baird Model 4-55 infrared spectrophotometer. Nmr analyses were performed on a Varian Model A-60 spectrophotometer using TMS as an internal standard. Refractive indices were measured on a Zeiss Opton refractometer thermostated at 20 ± 0.1°. Vpc separations and identifications were made using an F & M Model 720 dual-column gas chromatograph equipped with a thermal-conductivity detector using helium as a carrier gas. Separations, product compositions, and relative thermal conductivities were made using either 10% SE-30 silicone gum rubber on 60–80 Gas-Pack WAB columns or 15% Versamid 900 on 60–80 Gas-Pack WAB columns of various lengths and at appropriate temperatures. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich.

Registry No.—Isoprene, 78-79-5.

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[18] H. C. Brown and W. A. Murphey, *J. Amer. Chem. Soc.*, **73**, 3308 (1951).

[19] S. Bank, C. A. Rowe, Jr., A. Schriesheim, and L. A. Naslund, *ibid.*, **89**, 6897 (1967).

The Chemistry of Diazepines. The Photochemical Intramolecular 1,3-Dipolar Cycloaddition of Substituted 1-Ethoxycarbonyliminopyridinium Ylides[1]

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The photochemical intramolecular 1,3-dipolar cycloaddition of substituted 1-ethoxycarbonyliminopyridinium ylides produces 1H-1,2-diazepines. Structural elucidation of the diazepines was accomplished by spectral means and confirmed by Diels–Alder reactions with tetracyanoethylene (TCNE) and catalytic reduction.

Recently, increased attention has been paid to medium-sized cyclic nonbenzenoid heteroaromatic hydrocarbons such as azepines and oxepines.[2] Despite unabated interest in the theoretical and practical aspects of seven-membered heterocyclic chemistry, the diazepines have been incompletely defined, because until recently they have been known only in the form of condensed ring systems.[3] Recently, Streith, *et al.*,[4] reported the first synthesis of simple diazepines by the photochemical rearrangement of 1-ethoxycarbonyliminopyridinium ylides.

Independently, we have also reported the photochemical synthesis of 1H-1,2-diazepines by the same route.[1a] Since the photochemical behaviour of iminopyridinium ylides has not been so extensively investigated as that of aromatic amine oxides,[5] we have examined the solution-phase photolysis of α-, α,α′-, β-, and γ-substituted 1-ethoxycarbonyliminopyridinium ylides. This has led to a study of their catalytic reduction and their Diels–Alder reactions; the latter reactions appear to be the first in the diazepine series.

Results and Discussion

Syntheses of the Pyridinium Ylides.—The pyridinium ylides **3–11** were prepared by the reactions of α- and γ-picoline, 2,4-lutidine, β-picoline, 2,5-, 3,5-, 3,4-, and

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[1] (a) For the preliminary communication, see T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, 432 (1969). (b) Studies on Heteroaromaticity. XXXIII. Part XXXII of this series: T. Sasaki, T. Yoshioka, and Y. Suzuki, *Bull. Chem. Soc. Jap.*, **42**, 3335 (1969).

[2] For a recent brief review in the azepine field, see I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Amer. Chem. Soc.*, **90**, 5023 (1968); for the oxepin field, see E. Vogel, *et al.*, *Angew. Chem.*, **76**, 535 (1968).

[3] For a recent brief review, see T. Takase, *J. Syn. Org. Chem. Jap.*, **26**, 807 (1968).

[4] J. Streith and J.-M. Cassal, *Angew. Chem.*, **80**, 117 (1968); *Tetrahedron Lett.*, 4541 (1968); J. Streith, A. Blind, J.-M. Cassal, and O. Sigwalt, *Bull. Soc. Chim. Fr.*, 948 (1969).

[5] (a) P. L. Kumler and O. Buchardt, *Chem. Commun.*, 1321 (1968); (b) E. C. Taylor and G. G. Spence, *ibid.*, 1037 (1968); (c) C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron*, **25**, 295 (1969).