Base-Catalyzed Reactions. XXXII.[1a] Sodium- and Potassium-Catalyzed Side-Chain Alkenylation of γ-Alkylpyridines with Butadiene[1b]

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The sodium- and potassium-catalyzed side-chain alkenylation of γ-picoline and γ-propylpyridine with butadiene was investigated. The alkenylation was carried out at atmospheric pressure and at temperatures varying from 0 to 25°. The alkenylation was initiated by the anions produced from the reaction of the alkali metals with the alkylpyridines. The presence of metallic sodium or potassium caused polymerization of butadiene to high molecular weight polymers. The butenylation occurred exclusively on the alkyl carbon atom α to the pyridine ring and the double bond in the side chain was located at the γ position with respect to the pyridine ring. Mono-, di-, and triadducts were obtained. The skeletons of the produced alkenylpyridines were determined by means of selective hydrogenation and by comparing the alkylpyridines thus obtained with synthetic compounds. The structure of the alkenylpyridines was determined by infrared and nuclear magnetic resonance spectroscopy and the skeletal structures were confirmed by comparison with synthetic samples. The mechanism of the alkenylation reaction is discussed.

It has been established that alkylpyridines can undergo carbanion-catalyzed side-chain alkylation reactions similar to the side-chain alkylations of alkylbenzenes.[3-5] According to the proposed mechansim, the side-chain alkylation proceeds through an attack on the double bond in the olefins by 1-phenylalkyl (benzyl) or 1-pyridylalkyl (picolyl)[6] anion.

The reaction of conjugated dienes and of styrenes with alkylbenzene[5] has been studied in our laboratory and the structure of the compounds determined.[5,7] Wegler and Pieper[8] reported the reaction of butadiene with α-picoline, but they did not estabilsh the structure of the alkenylpyridine produced. The purpose of the present study was to obtain a better understanding of the side-chain alkenylation reactions by studying the reactions and the products of alkenylation of γ-alkylpyridines with butadiene.

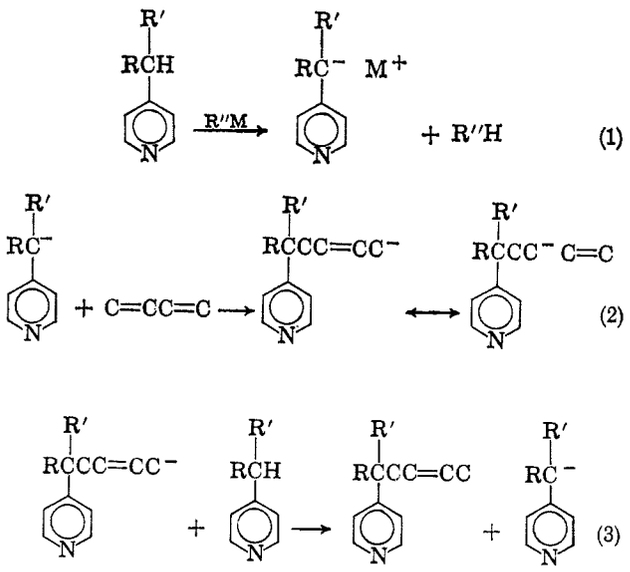
Discussion of Results

The reactions of γ-alkylpyridines with butadiene were carried out in the presence of catalytic amounts of sodium and potassium. The course of the reaction was followed by means of vapor phase chromatography. The separation of the individual compounds produced was accomplished by preparative gas chromatography and their structures were established by nmr and infrared spectroscopy; the skeletal structures were confirmed by selective hydrogenation. The alkylpyridines thus obtained were compared with synthetic samples.

It was established that the most suitable temperature range for the reaction is 0–20°. The rate of the alkenylation at −10° is slower but still satisfactory. Above 50°, a considerable amount of higher boiling material was produced. Structures of these compounds were not investigated, but they seem to contain more than one pyridine ring in the molecule.

It is essential that all of the metallic sodium or potassium be dispersed in the alkylpyridine to form the organoalkali solution, a reaction accompanied by a deep color change, before the butadiene is introduced to the reaction flask.

The mechanism of the butenylation of alkylpyridines can be explained by eq 1–3 where M = Na, K; R, R′ =



H, alkyl, alkenyl; and R″M = product of interaction of alkylpyridines with sodium or potassium.

The products obtained from the reaction of γ-picoline (PyC) and γ-propylpyridine with butadiene are given in Scheme I.

The relative rate of formation of the mono-, di-, and triadducts from γ-picoline and butadiene is given in Table I. For quantitative determination of the concentration of the various alkenylated pyridines, isopropyl- or *n*-butylcyclohexane was added to the γ-alkylpyridine as an internal standard for gas chromatographic analysis.

The di- and triadducts did not contain products of chain lengthening, similar to those observed in the alkenylation of toluene.[7a] Compounds with terminal double bonds were not observed, indicating that the protonation of the carbanions occurs at the terminal carbon atom owing to the greater electron density of

(1) (a) Paper XXXI: J. Shabtai and H. Pines, *J. Org. Chem.*, **30**, 3854 (1965). (b) Paper IV of the series, Alkylation of Heteroaromatics; for other papers, see ref 3.

(2) On leave of absence 1963–1965 from the University of Warsaw, Poland.

(3) (a) H. Pines and D. Wunderlich, *J. Am. Chem. Soc.*, **81**, 2568 (1959); (b) H. Pines and B. Notari, *ibid.*, **82**, 2209 (1960); (c) *ibid.*, **82**, 2945 (1960).

(4) E. Profft and F. Schneider, *Arch. Pharm.*, **289**, 99 (1956).

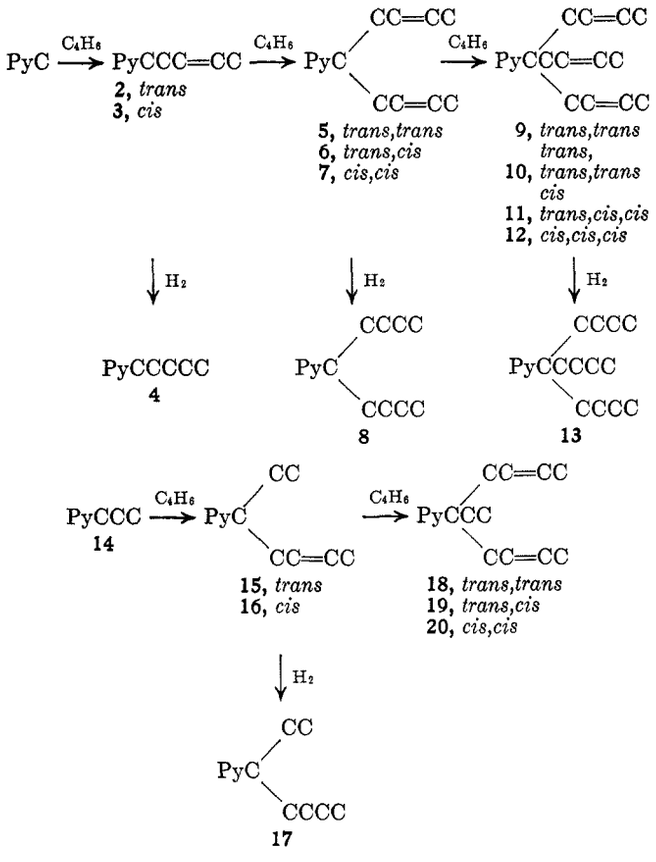
(5) For general review of the side-chain alkylation reaction, see H. Pines and L. Schaap, *Advan. Catalysis*, **12**, 117 (1960).

(6) Picolyl anion throughout the paper is defined as an anion on the α-carbon atom of the alkyl group in pyridine.

(7) (a) H. Pines and N. C. Sih, *J. Org. Chem.*, **30**, 280 (1965); (b) H. Pines and J. Shabtai, *ibid.*, **26**, 4220 (1961); (c) *ibid.*, **26**, 4225 (1961); (d) J. Shabtai, E. M. Lewicki, and H. Pines, *ibid.*, **27**, 2618 (1962); (e) J. Shabtai and H. Pines, *ibid.*, **29**, 2408 (1964).

(8) R. Wegler and G. Pieper, *Ber.* **83**, 6 (1950).

SCHEME I



the primary carbanion and/or to steric consideration. Products due to double bond migrations, similar to those observed in the case of phenylalkenes,[9] were also absent. This can be explained by the greater acidity of the picolyl anions over the benzyl anions.

The composition of butenylated γ-picoline as a function of time was determined in experiments made at atmospheric pressure and at 0–5° (Table I). During the first stages of butenylation the two isomers of 1-(γ-pyridyl)-3-pentene, *trans* **2** and *cis* **3**, were produced in a ratio **2**–**3** of 2.1:1.0 in the case of sodium and 2.3:1.0 in the case of potassium.

The dibutenylated product, 5-(γ-pyridyl)-2,7-nonadiene, gave a mixture of *trans,trans* **5**, *trans,cis* **6**, and *cis,cis* **7** isomers in ratios of 3.1:3.3:1.0 in the case of sodium and 5.6:4.7:1.0 when potassium was used as the catalyst. The formation of the dibutenylated product already could be observed when the yield of pentenylpyridine produced was only 1.5%, with respect to the starting γ-picoline.

Tributenylated products, which were formed when the yield of monobutenylated γ-picoline reached about 10%, consisted of four isomers. After selective hydrogenation they yielded 5-(γ-pyridyl)-5-*n*-butylnonane (**13**). On the basis of the structure of the diadducts and from the hydrogen uptake on selective hydrogenation and infrared spectrum, it should be assumed that the triadducts are composed of *cis* and *trans* isomers (**9**–**12**).

γ-*n*-Propylpyridine reacted with butadiene in a manner similar to γ-picoline (Table II). The monobutenylated product consisted of the two stereoisomers, *trans* **15** and *cis* **16**, which were formed in a ratio of 2.6:1.0. The dibutenylated product (**18**, **19**, and **20**) could be detected when the yield of monobutenylated product was 2%.

(9) N. C. Sih and H. Pines, *J. Org. Chem.*, **30**, 1462 (1965).

Competitive Butenylation

For a better understanding of the side-chain alkenylation reaction, the relative rates of butenylation of γ-picoline, γ-*n*-propylpyridine, and 1-(γ-pyridyl)-3-pentene were determined by means of competitive reactions. The butenylation was made by procedure b, at atmospheric pressure, using sodium as catalyst and an equimolar mixture of two alkylpyridines. Samples were withdrawn during the reaction at frequent intervals and the results are summarized in Table III.

The ratio of alkylpyridines used in the reaction will change during the course of butenylation, according to their rates of alkenylation; the ratio of butenylated product may also change because of further butenylation. In order to diminish these effects, only a small amount of the alkylpyridines was allowed to undergo butenylation.

The relative rate of butenylation of γ-propylpyridine (**14**) as compared with γ-picoline **1** was 4.8:1.0 at low conversation. This ratio was about the same 3.4:1.0) as calculated for the ethylation reaction of the two respective alkylpyridines.[3c] The relative ratio of butenylation of pentenylpyridines (**2** and **3**) and *n*-propylpyridine was 4.5:1.0 in favor of the former (Table III). From that it could be calculated that the relative rates of butenylation of pentenylpyridines **2** and **3** over γ-picoline (**1**) was 21.6:1.0 The estimated relative rates of butenylation of γ-picoline and pentenylpyridine could also be derived directly from the results of butenylation of γ-picoline. Since butenylated product

TABLE I

BUTENYLATION OF γ-PICOLINE[a]

Catalyst		Sample		Yield,[c] %		
Type	g-atom %[b]	no.	Time, hr	$PyC_2C{=}CC$ 2 and 3	$PyC(CC{=}CC)_2$ 5, 6, and 7	$PyC(CC{=}CC)_3$ 9, 10, 11, 12
Sodium	2	1	1.5	1.0[d]	0.2[f]	0
		2	3.25	4.3	2.2	0
		3	5.25	6.1	6.0	Traces
		4	6.0	6.8	9.5	0.7
		5	6.33	7.4	12.0	1.0
		6	7.5	8.2	22.1	3.2
Sodium	5	1	0.75	1.6[d]	0	0
		2	3.0	8.0	13.8[f]	1.2
		3	3.5	14.3	40.3	4.7
		4	4.0	13.2	45.1	6.4
		5	4.5	12.0	54.8	6.8
		6	5.0	10.2	69.2	
Potassium	~1	1	0.25	0.1[e]	Traces[g]	0
		2	0.6	0.3	0.2	0
		3	1.0	0.5	0.6	0
		4	2.5	0.5	0.7	0
		5	5.0	4.8	4.0	Traces
Potassium	5	1	0.25	2.1[e]	0.6[h]	0
		2	0.50	2.2	0.7	0
		3	1.0	2.9	0.9	0
		4	1.5	3.2	1.0	0

[a] The reactions were carried out at 0–5°. The conditions and the composition of the reagents are given in the Experimental Section. [b] g-atom % based on the moles of γ-picoline used in the reaction. [c] Based on γ-picoline used in the reaction. The boldface numbers refer to compounds given in text. [d] Ratio of **2**–**3** = 2.1:1.0. [e] Ratio of **2**–**3** = 2.3:1.0. [f] Ratio of **5**–**6**–**7** = 3.1:3.3:1.0. [g] Ratio of **5**–**6**–**7** = 5.6:4.7:1.0. [h] Ratio of **5**–**6**–**7** = 5.6:4.7:1.0.

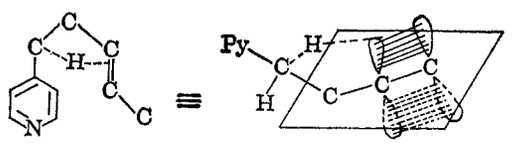
TABLE II

BUTENYLATION OF γ-*n*-PROPYLPYRIDINE[a]

Sample	Time,	Yield, %	
no.	hr	$PyC(C_2)(CC{=}CC)$ 15 and 16	$PyC(C_2)(CC{=}CC)_2$ 18, 19, and 20
1	0.5	5.8[c]	0.2
2	1.1	8.3	0.3
3	1.5	10.8	0.4
4	2.0	11.0	0.5
5	2.6	12.6	0.9
6	3.0	13.8	1.1

[a] Sodium, 5 g-atom %, based on the moles of *n*-propylpyridine used. For explanations, see footnotes to Table I. [b] Ratio of **15**–**16** = 2.6:1.0.

was formed, there occurred a competitive reaction between it and the starting picoline. Taking into consideration their respective concentrations at certain intervals and the increment concentration of their butenylation products, on successive time intervals it was thus estimated that pentenylpyridines were butenylated about 45 times faster than picoline. These differences in the rate of alkenylation of alkyl- and butenylpyridines could best be explained by the greater acidity of the pentenylpyridines owing to a π-electron bonding of the picolyl hydrogen with the double bond of the alkenyl group.



Structure Determination

The butenylated pyridine was distilled into numerous fractions and the isomeric butenylpyridines were isolated in pure form by means of preparative gas chromatography. A portion of the mixture of the double-bond stereoisomers was selectively hydrogenated to the corresponding alkylpyridines at atmospheric pressure using palladium catalyst. From the amount of hydrogen absorbed during hydrogenation, the number of double bonds per molecule was determined (Table IV). The infrared and nmr spectra of the alkyl- and alkenylpyridines were taken (Tables IV and V).

Pentylpyridine (**4**) was also prepared independently by treating γ-picoline with the corresponding *n*-butylbromide in the presence of sodium amide in liquid ammonia.[10] The physical constants, gas chromatographic analysis, and the infrared and nmr spectra of the synthesized pentylpyridine were identical with those obtained by selective hydrogenation of the pentenylpyridines. Pyridines **15** and **16** were also obtained by catalytic ethylation of mixture of **2** and **3**.

The position of the double bonds of the alkenylpyridines was established by nmr spectra. Each high-resolution spectrum obtained could be interpreted by one, and only one, structural formula and thus it was possible to establish unequivocally the structures of the alkenylpyridines.

The various protons were determined from the position of the resonance bands and their multiplicity.[11] Characteristic protons are listed in Table IV. The total number of aliphatic protons and the number of protons causing multiplets were determined from the integration curve. The α- and the β-pyridine protons were taken as internal standards for the integration.

In all the compounds, the absorption bands of the two α-pyridine ring protons, at δ 8.4–8.6 ppm, and the two β-pyridine protons, at 7.0–7.2 ppm, were present,

(10) H. C. Brown and W. A. Murphey, *J. Org. Chem.*, **73**, 3308 (1951).

(11) (a) "High Resolution NMR Spectra," Varian Associates, Palo Alto, Calif.; (b) L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, England, 1959; (c) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).

TABLE III

COMPETITIVE BUTENYLATION OF γ-ALKYL- AND ALKENYLPYRIDINES

			γ-Pyridines					
			Monobutenyl			Dibutenyl		
			Yield,[b] %		Ratio	Yield,[b] %		Ratio
Alkylpyridines[a]	Sample no.	Time, hr	A	B	A–B reacted	A	B	A–B reacted
A. γ-*n*-Propylpyridine	1	0.5	6.9	1.4	4.9	0.2	0.4	0.5
	2	1.0	10.8	2.3	4.7	0.3	0.7	0.4
B. γ-Picoline	3	1.66	14.4	3.1	4.6	0.4	1.5	0.3
	4	2.0	15.3	3.4	4.5	0.6	1.7	0.4
	5	2.5	16.2	3.9	4.2	1.0	1.9	0.5
	6	3.0	19.8	4.7	4.2			
A. γ-Pentenylpyridine	1	0.5	3.5	0.8	4.5			
B. γ-*n*-Propylpyridine	2	1.0	4.1	0.9	4.5			

[a] Equimolar ratio of compounds A and B were used. Sodium catalyst amounted to 5 g-atom % based on the total moles of A and B; temperature, 0–5°. [b] The yields are given in mole % respective to the starting corresponding pyridines.

TABLE IV

THE CHARACTERIZATION OF THE γ-ALKYL- AND γ-ALKENYLPYRIDINES

						No. of characteristic protons from nmr spectra[a–c]					
							Methyl groups		Methylenic group		
Compd	R	Formula	Bp (mm), °C	n^{20}D	Hydrogen uptake,[a] moles of H_2/mole of PyR[d]	Aliphatic protons	CH_3CC– δ 0.7– 0.9	CH_3C=C δ 1.3– 1.7	CH_2C=C δ 2.2– 2.4	Olefinic protons δ 5.2– 5.7	Picolyl protons[g] δ 2.4– 2.7
2	$-(CH_2)_2CH$=$CHCH_3$ (*trans*)	$C_{10}H_{13}N$	103–105 (8)	1.513[f]	1.04	9	0	3 d	2	2	2
3	$-(CH_2)_2CH$=$CHCH_3$ (*cis*)	$C_{10}H_{13}N$		1.513[f]		9	0	3 d	2	2	2
4	$-(CH_2)_4CH_3$	$C_{10}H_{15}N$	105 (10)	1.4420		11	3 t	0	0	0	2
5	$-CH(CH_2CH$=$CHCH_3)_2$ (*trans,trans*)	$C_{14}H_{19}N$		1.5141		15	0	6 d	4	4	1
6	$-CH(CH_2CH$=$CHCH_3)_2$ (*cis,trans*)	$C_{14}H_{19}N$	118–120 (2)	1.5148	2.12	15	0	3 d + 3 d[e]	4	4	1
7	$-CH(CH_2CH$=$CHCH_3)_2$ (*cis,cis*)	$C_{14}H_{19}N$		1.5161		15	0	6 d	4	4	1
8	$-CH[(CH_2)_3CH_3]_2$	$C_{14}H_{23}N$									
9–12	$-C(CH_2CH$=$CHCH_3)_3$	$C_{18}H_{25}N$	140–141 (2)	1.522		19	6 t	0	0	0	1
13	$-C[(CH_2)_3CH_3]_3$	$C_{18}H_{31}N$		1.4921		27	9 t	0	0	0	0
15	$-CH(C_2H_5)(CH_2CH$=$CHCH_3)$ (*trans*)	$C_{12}H_{17}N$	85–87 (1.5)	1.5055	1.03	13	3 t	3 d	2	2	1
16	$-CH(C_2H_5)(CH_2CH$=$CHCH_3)$ (*cis*)	$C_{12}H_{17}N$		1.507		13	3 t	3 d	2	2	1
17	$-CH(C_2H_5)[(CH_2)_3CH_3]$	$C_{12}H_{19}N$		1.4875		15	6 t	0	0	0	1

[a] In all the compounds listed, the nmr bands of the two β-pyridine protons, δ 7.0–7.2 ppm, and the two α-pyridine protons, δ 8.4–8.6 ppm, are present. [b] s singlet, d doublet, t triplet. [c] δ values are given in ppm; tetramethylsilane (TMS) was used as reference. [d] PyR corresponds to alkenylpyridines. [e] Separate doublets of *cis* and *trans* chains. [f] ±0.002. [g] At carbon atoms connected to the pyridine ring.

indicating that the substitution occurred at the γ-pyridine side chain.

The most significant resonance bands were of substituents at the C=C group. The bands of the olefinic protons absorbing at δ 5.2–5.7 ppm indicate the substitution of the double bond. The 1.3–1.7-ppm band with a doublet demonstrated that the carbon atom connected to the methyl group, CH_3C=C, contained one proton.

The protons at the γ-picoline carbon atom, connected to the pyridine ring, absorb in the range 2.4–2.7 ppm; from the number of the protons the substitution at this atom was determined. The $-CH_2-$ groups linked with a saturated carbon atom gave multiplet broad bands with maxima located at 1.5–1.7 and 1.1–1.3 ppm.

cis and *trans* isomers of the alkenylpyridines were differentiated by the presence and absence of the specific bands in the infrared spectra of the alkenylpyridines before and after hydrogenation, respectively: *trans* 970–960 cm^{-1}, *cis* 1310–1295 cm^{-1} and about 690 cm^{-1} (Table V). The differentiation between the *cis* and *trans* isomers was confirmed by the nmr spectra. The resonance band of the methyl group adjacent to the double bond (CH_3C=C—) in the *cis* isomer is shifted about 0.05–0.10 ppm upfield with reference to the corresponding band of the *trans* isomer.[11]

Experimental Section

Reagents.—γ-Picoline and γ-*n*-propylpyridine were purchased from Reilly Tar Co. The material was dried over barium oxide and distilled in a nitrogen atmosphere on a Podbielniak Heligrid column, 1.5 m long. The alkylpyridines used in the reaction were over 99.5% pure as adjudged by gas chromatography. Isopropyl- and *n*-butylcyclohexane, used as internal standards, were obtained by catalytic hydrogenation at 150° of the corresponding alkylbenzene. The initial pressure of hydrogen was 130 atm and the catalyst was nickel (Kieselguhr). Butadiene was obtained from Matheson Co. In order to avoid contamination with stabilizers, the butadiene which was over 99.5% pure was removed from the pressure vessel in the form of gas.

Preparation of Catalysts and General Procedure.—The preparation of the catalyst and the alkenylation reaction was performed in a three-necked flask of 50-ml capacity. The flask was equipped with a specially designed drum-shaped high-speed stirrer and a condenser to which a potassium hydroxide drying tube was attached.

The alkylpyridine (0.1 *M*), was admixed with 5% by weight of *n*-butylcyclohexane or isopropylcyclohexane as an internal standard for vpc analysis. About 0.005 g-atom of either sodium or potassium was placed in the reaction flask under a blanket of dry nitrogen and the remaining neck of the flask was closed with a rubber septum to allow the later addition of diene and removal of sample. The sodium reacted with alkylpyridines at room

TABLE V

INFRARED SPECTRA OF α-ALKENYLPYRIDINES[a]

2 -CCC=CC *trans*	3 -CCC=CC *cis*	4 -CCCCC	5 *trans,trans*	6 -C<CC=CC / CC=CC *trans,cis*	7 *cis,cis*	8 -C<CCCC / CCCC	15 -C<CC / CC=CC *trans*	16 -C<CC / CC=CC *cis*	17 C<CC / CCCC
3075 w	3070 w	3070 mw	3075 m	3075 mw	3075 mw	3070 mw	3070 m	3070 m	3070 mw
3030 m	3030 m	3030 mw	3030 ms	3030 ms	3030 ms	3030 mw	3035 s	3030 s	3030 m
2965 w	2970 w	2960 s	2965 ms	2965 m	2965 mw	2960 s	2965 s	2965 s	2965 s
			2950 ms	2950 m	2950 m				
2925 mw	2940 mw	2935 s	2925 s	2925 ms	2925 mw	2935 s	2935 s	2935 s	2935 s
2860 w	2870 w	2870 ms	2860 ms	2860 m	2860 mw	2860 s	2860 s	2880 s	2870 s
1940 w	1940 w	1940 w	1940 w	1935 w		1940 w	1940 w	1940 w	1940 w
						1740 w	1740 w	1740 w	1740 w
	1670 w		1670 w	1670 w	1660 w			1665 mw	
			1645 mw	1650 w			1650 w		
1600 s	1600 s	1600 s	1600 s	1600 s	1600 s	1600 s	1600 s	1600 s	1600 s
1560 mw	1560 mw	1560 mw	1560 m	1560 mw	1560 mw	1560 w	1560 m	1560 ms	1560 m
		1530 w		1530 w					1530 w
1500 mw	1510 mw	1500 mw	1500 mw	1500 mw	1500 w	1500 mw	1500 m	1500 m	1505 mw
1460 m	1440 m	1465 m	1450 ms	1450 m	1450 m	1460 ms	1450 ms	1460 ms	1470 ms
			1440 s	1440 m	1440 m		1440 s	1450 ms	
								1440 ms	
1410 s	1410 s	1410 ms	1410 s	1410 ms	1415 ms	1410 s	1410 mw	1410 s	1410 s
		1380 mw		1380 mw		1380 m	1380 m	1380 m	1385 m
1375 mw	1375 mw		1375 m		1375 mw		1375 mw	1370 m	
						1340 w	1340 mw	1335 mw	1335 w
	1325 w			1325 w	1325 w			1320 w	
1225 mw	1225 mw	1225 mw	1225 m	1225 mw	1225 w	1225 mw	1225 m	1225 ms	1225 mw
		1115 wb	1120 wb	1130 wb		1125 w	1135 w	1135 w	1140 w
		1105 w		1120 wb		1115 w			
1073 w	1073 w	1073 w	1073 m	1073 mw	1073 w	1073 mw	1073 m	1073 m	1077 mw
			1040 wb	1040 w			1040 w	1040 w	1040 w
997 ms	997 ms	997 m	997 ms	997 m	997 m	997 m	997 ms	997 s	998 m
965 sb			965 sb	965 msb			965 s		
						955 w	950 m	948 mw	940 w
920 mb	918 mb		918 msb	918 mwb	918 wb		912 w	915 w	
						895 w	875 w	875 w	875 w
							850 w	850 w	
	837 mw	832 mwb	825 sb	820 ms	825 ms	825 msb	825 msb	825 s	820 s
	810 msb	800 msb					818 m	818 w	
	780 w	770 wb						795 m	
						785 w	775 mw	775 mw	786 mw
755 w				750 wb	755 mw	755 w	755 mw	757 m	757 w
							742 m	747 ms	746 mw
		728 mwb				730 m			732 m
	700 msb			702 mb	710 msb			710 sb	

[a] The peaks are referred to according to their intensities with respect to the strongest peak in the spectrum: s strong, ms medium strong, m medium, mw medium weak, w weak (with intensities 60–100, 60–80, 40–60, 20–40, and below 20%, respectively); b broad (half-width more than 15% of peak height).

temperature, forming a deep dark red solution with picoline or deep purple with γ-*n*-propylpyrdine.[4] Potassium, if exposed to air, enters into solution slowly; in order to make an active catalyst this may mecessitate the heating of the contents of the flask to 45° for about 30 min. In order to prevent the polymerization of the butadiene, it is important not to have any sodium or potassium metal present upon addition as stated previously.

The high-speed stirrer was replaced by a Teflon-coated magnetic stirring bar and the drying tube was replaced by a connection to a gas buret containing the butadiene. The flask was immersed in an ice bath and the rate of the absorption of butadiene could be read from the calibrations on the gas buret. Samples were withdrawn for analysis during the reaction through the rubber septum by means of a syringe. Samples (0.05 ml) were withdrawn at definite intervals, injected into 0.1 ml of methanol to decompose the organometallic compounds, and analyzed by means of gas chromatography. After the reaction reached the required point, the catalyst was decomposed by the addition of methanol until the solution became colorless or pale yellow and the product was then subjected to distillation.

Spectroscopic Analyses.—The infrared spectra of the pyridines, purified by gas chromatography, were taken with a Baird infrared spectrophotometer, Model 4-55, calibrated at 11.03, 8.46, 6.69, 6.24, 5.54, and 5.13 μ with a polyethylene film. Samples of 8–10 μl were placed as films between two sodium chloride plates using air as reference. Nmr spectra were obtained on a Varian A-60 spectrometer. Samples varying from 20 to 50 μl in carbon tetrachloride, total volume 400 μl, with an addition of 1–2 drops of tetramethylsilane as reference were used. Refraction indices were measured on the Zeiss Opton refractometer with a thermostat at 20 ± 0.1°. All samples used for analysis were of purity greater than 95%.

Vapor Phase Chromatography.—Analyses were performed with F & M Model 720 dual-column gas chromatograph with a thermal conductivity detector, using helium as carrier gas. The analytical columns used are listed in Table VI.

The yields of mono-, di-, and trialkenylated pyridines were determined by calculating the peak areas in relation to the internal standard, isopropyl- or *n*-butylcyclohexane, added in known amounts before alkenylation. The areas of resolved peaks were determined by a triangulation method; in the case of overlapped peaks, the σ method was applied.[12]

The composition of the product obtained from the reaction of γ-picoline with butadiene was analyzed on column A, with linear

(12) K. C. Bartlett and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960).

TABLE VI

DESCRIPTION OF THE VAPOR PHASE CHROMATOGRAPHIC COLUMNS

Column	Liquid phase	Weight, %	Solid support	Mesh size	Column: Length, m	Column: o.d., in.
A	Gum rubber phenyl methyl GE-SE-52	10	Chromosorb P	30–40	1.5	1/4
B	Gum rubber phenyl methyl GE-SE-52	15	GAS-Pack WAB	60–80	1.5	1/4
C	Reoplex 400	15	GAS-Pack WAB	60–80	1.5	1/4
D	Versamid 900	10	GAS-Pack WAB	60–80	1.5	1/4
E	Gum rubber phenyl methyl GE-SE-52	12	GAS-Pack WAB	60–80	2.4	3/8
F	Reoplex 400	15	GAS-Pack WAB	60–80	3.9	3/8
G	Versamid 900	15	GAS-Pack WAB	60–80	2.3	3/8

temperature program of 5°/min between 80 and 280° and helium flow of 100 ml/min, and on column D at 210°. For the determination of the ratio of the *cis* and *trans* isomers, column C was used and the analytical conditions were gas flow 100 ml/min, temperature 140° for compounds **2** and **3** and 160° for **5**, **6**, and **7**. For the butenylated γ-propylpyridine, column B, temperature 160°, helium flow of ml/min, also was used.

For preparative separation and purification of the various alkenylpyridines, the following conditions were used (compounds, column, temperature, helium flow in ml/min): **2**, **3**, **4**, **15**, **16**, and **17**, G, 185°, 100, and G, 160–170°, 75–80; **5**, **6**, and **7**, G, 200°, 100, and F, 200°, 50; **13**, G, 220°, 80. The product obtained from each separation was tested again on vpc and when necessary the compound were repurified. The relative retention times of the alkyl- and alkenylpyridines will be described separately.[13]

Registry No.—**2**, 13573-41-6; **3**, 13573-42-7; **4**, 2961-50-4; **5**, 13573-44-9; **6**, 13573-45-0; **7**, 13628-62-1; **8**, 2961-47-9; **9**, 13573-47-2; **10**, 13573-48-3; **11**, 13573-49-4; **12**, 13573-50-7; **13**, 13573-51-8; **15**, 13573-52-9; **16**, 13573-53-0; **17**, 13573-54-1; butadiene, 685-20-1.

(13) J. Oszczapowicz, J. Golab, and H. Pines, to be published.