

Base-Catalyzed Reactions. XXXVI.¹ Sodium- and Potassium-Catalyzed Reactions of Selected 4-Alkylpyridines with Isoprene

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The addition of various 4-alkylpyridines to isoprene in a sodium- or potassium-catalyzed reaction has been observed. The pyridines selected for this study were 4-methyl-, 4-ethyl-, 4-*n*-propyl-, 4-isopropyl-, and 4-*sec*-butylpyridine. The reaction proceeds readily at 0–25° via a Michael-type addition mechanism to yield mono-, di-, and triaddition products. The addition of isoprene occurs exclusively on the alkyl carbon atom α to the pyridine ring, and no double-bond isomerization was noted in the product formed. In all cases, tail addition predominates over head addition, and the ratios of the products seem to be determined by both the relative stabilities of the resultant carbanions and the steric hindrance to addition. The alkenylation reaction is discussed, as is the determination of structure of the produced alkenylated pyridines by various physical and chemical means. The nmr spectra of most head addition products show a diamagnetic upfield shift for the interior methyl group. These same addition products also fail to undergo hydrogenation under conditions employed to hydrogenate the tail-addition isomers.

The reaction of olefins with alkylaromatics changes markedly with the type of catalyst and/or experimental conditions used. A good example of this is the reaction of toluene with propylene. With an acid catalyst, the main product is *p*-cymene, the result of ring alkylation;³ however, under free-radical conditions, side-chain alkylation is found and *n*-butylbenzene is produced,⁴ while a base catalyst produces isobutylbenzene, also a product of side-chain alkylation.⁵ The side-chain alkylations of alkylaromatics catalyzed by alkali metals, in which the actual catalyst is an organoalkali metal complex, have been under intensive study in our laboratories. The initial study concerned the alkylation of alkylbenzenes having a benzylic hydrogen.^{6,7} It was necessary to initiate these reactions with a promoter and to perform the reactions in an autoclave at temperatures varying from 150–200°, depending upon the reactants. When toluene was added to isoprene, only the mono-addition products were examined as further alkenylation occurred to give chain-lengthening isomers, presumably because addition to isoprene is faster than protonation.⁸ Even though the possibility of 1,2 addition to isoprene exists, as has been found in polymerization studies of isoprene,⁹ only 1,4-addition products were found in this case, which may be attributed to steric hindrance to protonation.

The first alkylations of 2- and 4-alkylpyridines were performed using ethylene at temperatures of 130–160°.¹⁰ Recently, the alkenylation and aralkylations of various 2- and 4-alkylpyridines with butadiene and styrenes have been reported.^{11,12} The alkenylation of 4-picoline with butadiene proceeded to give mono-, di-,

and triaddition products, all from substitution on the picolyl carbon.

The present work was initiated to give further insight into the alkenylation mechanism. Since isoprene has an unsymmetrical structure, and can thus add in two different ways, it should be more instructive in following the reaction pathway. It was also desirable to compare the results of this study with the analogous additions of alkylbenzenes to isoprene.⁸ Complete conversion of alkylpyridines to products was found when care was taken to purify the reactants. In the present work, 4-picoline, 4-ethylpyridine, 4-*n*-propylpyridine, 4-isopropylpyridine, and 4-*sec*-butylpyridine were used as the aromatics, and product structure determinations were made by both physical and chemical means.

Results and Discussion

The addition of various 4-alkylpyridines to isoprene was carried out in a pseudohomogeneous solution of dispersed catalytic amounts of metallic sodium or potassium. The reactions were observed to proceed at 0° for 4-picoline, 4-ethylpyridine, and 4-*n*-propylpyridine, but no addition product was produced with 4-isopropylpyridine or 4-*sec*-butylpyridine until the reaction mixture was warmed to room temperature. To obtain complete conversion of the pyridines to products, it was essential that all of the materials be distilled, dried over molecular sieves, and then redistilled immediately before use. If the dispersion of the alkali metal was aided by applying heat, varying amounts of side products, probably dipyrityls, were produced, and complete conversion of the pyridines to products was no longer found. The dispersion of potassium was always more difficult than that of sodium metal.

When sodium is dissolved in substituted pyridines, a radical anion is formed,¹³ and thus it is proposed that the mechanism of metalation goes through the radical anion as discussed previously.¹⁴ The radical anion could then abstract a proton, leading directly to the picolyl anion,¹⁵ or could go through a ring-metalated anion in a kinetically controlled sequence followed by conversion to the more thermodynamically stable α

(1) (a) For paper XXXV, see N. E. Sartoris and H. Pines, *J. Org. Chem.*, **34**, 2119 (1969). (b) Paper VII of the series Alkylation of Heteroaromatics. For paper VI, see ref 1a.

(2) Monsanto Predoctoral Fellow, 1965–1966; Ethyl Corp. Predoctoral Fellow, 1967–1968.

(3) S. H. Patinkin and B. S. Friedman in "Friedel-Crafts and Related Reactions," Vol. II, part I, G. A. Olah, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, pp 9–16 and 149–151.

(4) H. Pines and J. T. Arrigo, *J. Amer. Chem. Soc.*, **79**, 4958 (1957).

(5) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956).

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

(7) J. Shabtai and H. Pines, *J. Org. Chem.*, **30**, 3854 (1965), and references cited therein.

(8) H. Pines and N. C. Sih, *ibid.*, **30**, 280 (1965).

(9) See C. E. H. Bawn and A. Ledwith, *Quart. Rev. (London)*, **16**, 361 (1962).

(10) H. Pines and B. Notari, *J. Amer. Chem. Soc.*, **82**, 2209 (1960).

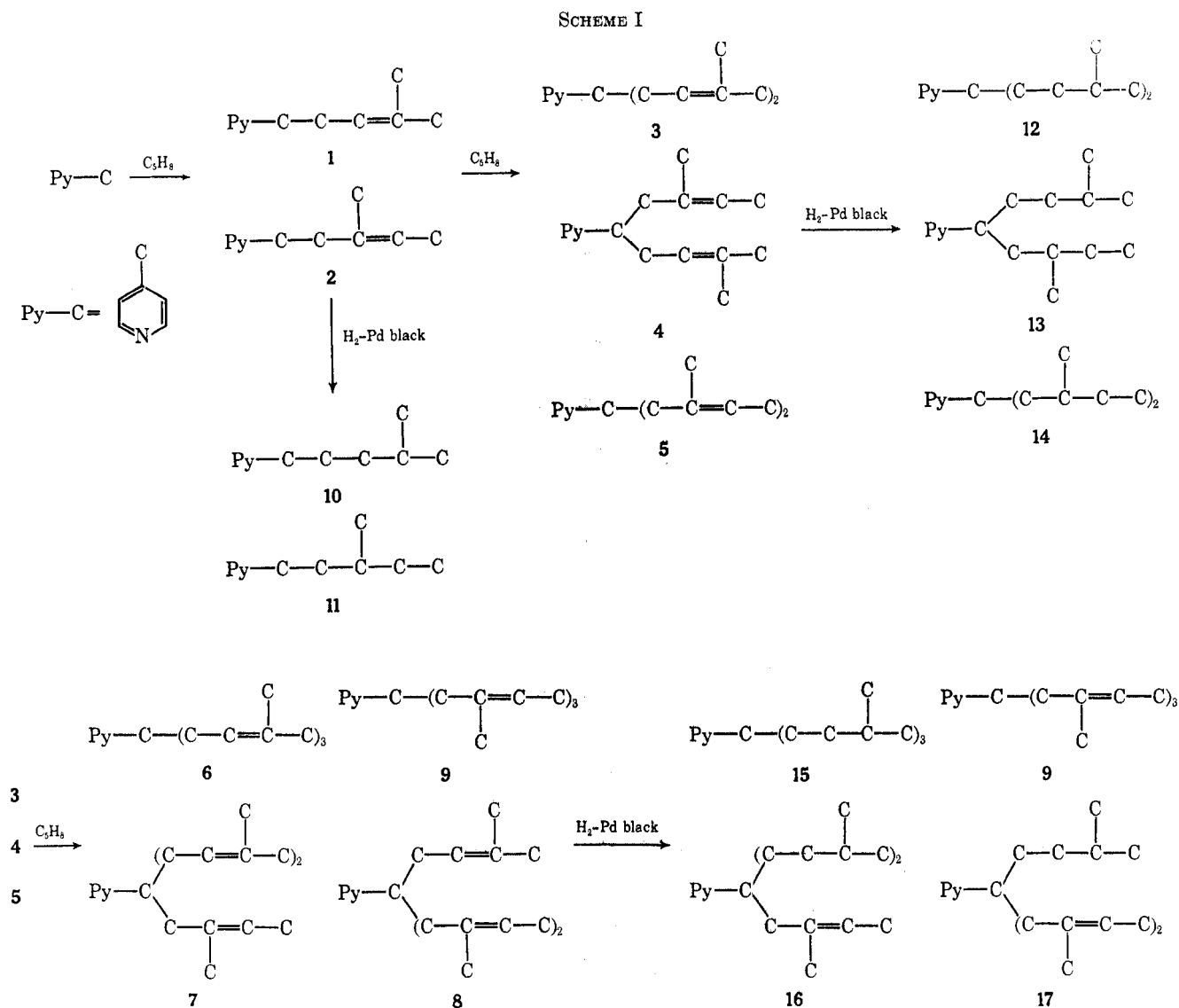
(11) H. Pines and J. Oszczapowicz, *J. Org. Chem.*, **32**, 3183 (1967).

(12) H. Pines and N. E. Sartoris, *ibid.*, **34**, 2113 (1969).

(13) M. Itoh and S. Nagakura, *Tetrahedron Lett.*, 417 (1965).

(14) B. Stipanović and H. Pines, *J. Org. Chem.*, **34**, 2107 (1969).

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



bon analogs.¹⁷ The product ratio then agrees with the concept that the less reactive reagent shows the greater selectivity. In the case of 4-ethylpyridine, examination of molecular models indicates that the terminal methyl group can situate itself so that it does not sterically hinder the addition of isoprene and, being a more reactive anion than picoline, it thus gives a slightly lower A/B ratio. The selectivity for 4-*n*-propylpyridine is greater, since the extra ethyl group is situated so that head addition to give B is sterically hindered, whereas tail addition to give A is not affected; this point is further discussed in the following paper.¹⁸ The most reactive anions would be those of 4-isopropylpyridine and 4-*sec*-butylpyridine. Using a potassium ion catalyst, 4-isopropylpyridine reacts about as fast and selectively as 4-ethylpyridine, but 4-*sec*-butylpyridine reacts much slower and again shows steric hindrance to head addition as did 4-*n*-propylpyridine.

In general, with sodium as a catalyst the anion seems to be less reactive and the selectivity greater, thus giving larger proportions of tail-addition products (A) than when potassium is used as a catalyst. The

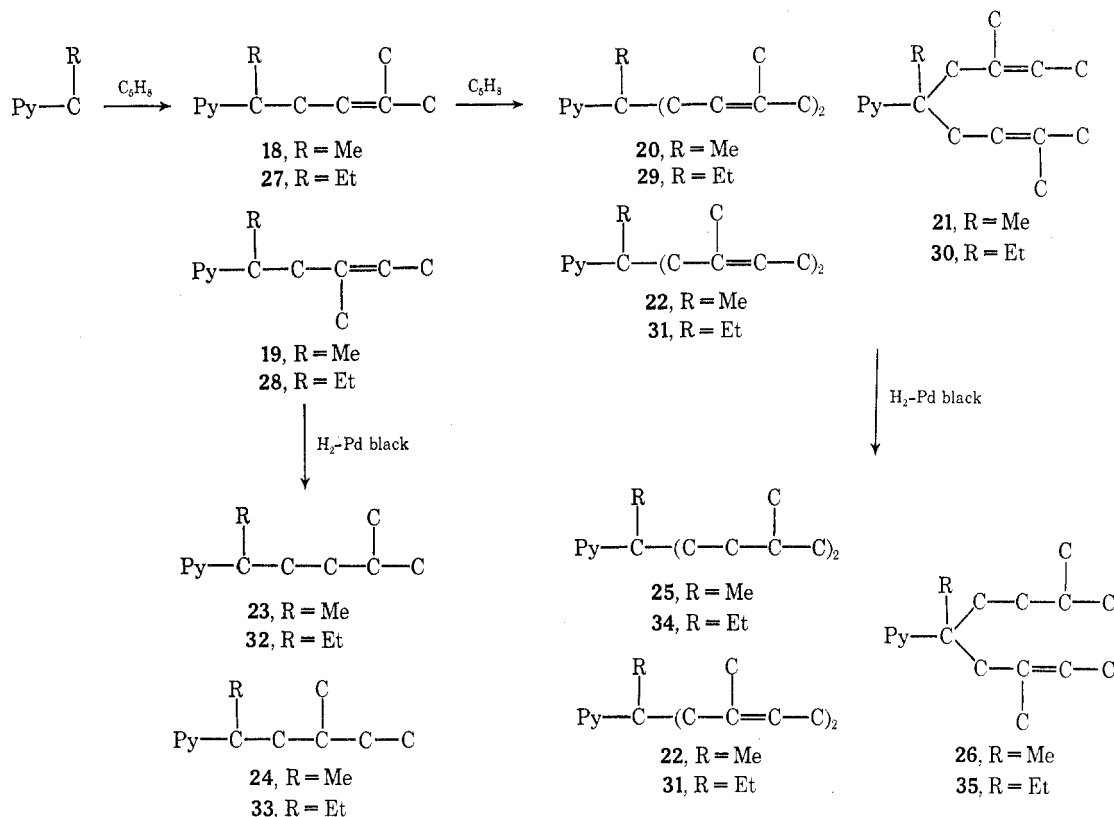
product ratios of A/B found when sodium was used were 1.6:1 for 4-picoline, 2.1:1 for 4-ethylpyridine, *ca.* 2:1 for 4-*n*-propylpyridine, 3:1 for 4-isopropylpyridine, and 9:1 for 4-*sec*-butylpyridine. Tables I-III also show that the reaction rates proceed in the following order, starting with the most reactive alkylpyridine: 4-ethylpyridine > 4-*n*-propylpyridine > 4-isopropylpyridine > 4-methylpyridine > 4-*sec*-butylpyridine. These results compare favorably with those found when competitive reactions are run.¹⁸

It should be noted that in all cases the product distribution percentages are applicable only for the particular molar ratios of reactants used. Also, the reaction times given in the tables are those derived from one experiment and are generally reproducible for the reactions in which all reactants are purified. The reactions were run using *ca.* 5 g-atom % of dispersed alkali metal and a 25-50% excess of isoprene based on complete reaction of the 4-alkylpyridine to give the fully substituted product; *i.e.*, 1 mol of 4-ethylpyridine was treated with 2.5-3.0 mol of isoprene. The reactions were followed in all cases to 100% conversion of the alkylpyridine to products, and in many cases the reaction was followed longer to see if the product distribution changed.

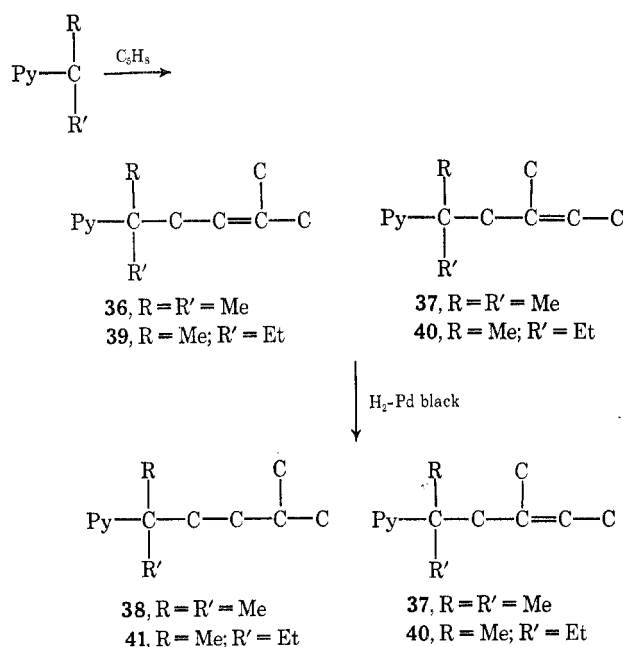
(17) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 1-27 and references cited therein.

(18) W. M. Stalick and H. Pines, *J. Org. Chem.*, **35**, 422 (1970).

SCHEME II



SCHEME III



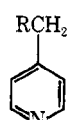
As in the previous work,¹¹ no double-bond isomerization was noticed in the products found. In addition, unlike the reactions of isoprene with alkylbenzenes,⁸ no chain lengthening was observed when two isoprenoid units were added. While the present study was in progress, a report of the sodium-catalyzed addition of isoprene to 3-picoline at 140° was made; however, the authors only reported finding the tail-addition isomers.¹⁹

(19) Yu. I. Chumakov and V. M. Ledovskikh, *Ukr. Khim. Zh.*, **31**, 506 (1965); *Chem. Abstr.*, **63** 5594a (1965).

The mono-, di-, and triaddition products were roughly separated by distillation. To ease the separation of similarly boiling hydrogenated isomers, selective hydrogenation was performed in the presence of a palladium oxide catalyst. This method selectively hydrogenated only the tail-addition isomers while leaving the head-addition units unsaturated. This hydrogenation procedure was effective on all compounds having a fully substituted picolyl carbon (see Schemes I-III). It was not possible to separate the products formed when a secondary anion was added to isoprene; *i.e.*, **3**, **4**, and **5** were inseparable, as was **20** from **22** and **29** from **31**. In these cases the product ratios were determined by nmr (see below). The structural determinations of the products were made on the pure compounds separated by means of preparative gas chromatography. The physical constants of the reaction products and their corresponding hydrogenated species are given in Table IV. A few of the hydrogenated isomers were compared with products synthesized by independent means.¹⁸ As the infrared spectra were all consistent with the compounds formed and also similar to one another, they will not be discussed. The main tool used for structural determinations was the nmr, and the results are discussed in the following section.

Discussion of Nmr Data.—The nmr spectra are quite definitive for the compounds proposed, and it is possible to divide them into four main classes (see Table V). In all cases the two α protons of pyridine gave resonance peaks at δ 8.3–8.6 ppm, and the two β -proton peaks were located at δ 6.95–7.2 ppm. Since these four pyridine protons were always present, they were taken as internal standards for integration and will not be further discussed.

TABLE II
 PENTENYLATION OF 4-ETHYL- AND 4-*n*-PROPYLPYRIDINE

				Conversion of alkyl- pyridine, %	Yield, ^a %				
R	Catalyst	Sample no.	Time, hr		Monoaddition 18 + 19 or 27 + 28	Diaddition			
					20 or 29	21 or 30	22 or 31		
RCH ₂ 	Sodium	1 ^b	0.5	30	100 ^c	
		2	1.0	66	96	2	2	..	
		3	1.5	93	84	9	7	Trace	
		5	3.5	100	52	27	19	2	
		1 ^b	0.5	46	95 ^d	2	3	..	
	Potassium	2 ^b	1.0	70	87	6	7	..	
		5	2.5	100	70	14	15	1	
		6	5.3	100	15	40	40	5	
		Sodium	1 ^b	0.5	45	100 ^e
			3 ^b	1.5	82	100
4	2.0		100	100		
5	3.0		100	98	2		
6	21.0		100	77	20	3	..		
Potassium	1 ^b	0.5	8	100 ^e		
	3	1.5	55	100		
	4	2.0	78	100		
	5	2.5	100	91	6	2	..		
	7	5.8	100	80	15	5	..		
10	20.0	100	59	28	13	Trace			

^a Compounds 18–22 and 27–31 are the products of pentenylation of 4-ethylpyridine and 4-*n*-propylpyridine, respectively. ^b Reaction was run at 0° for these samples and then warmed to 20–25° for subsequent samples. ^c From nmr it was found that 68% of the monoadduct was 18 and 32% was 19. ^d From nmr it was found that 55% of the monoadduct was 18 and 45% was 19. ^e From nmr it was estimated that about 60–70% of the monoadduct was 27 and 30–40% was 28.

 TABLE III
 PENTENYLATION OF 4-ISOPROPYL- AND 4-*sec*-BUTYLPYRIDINE

				Conversion of alkylpyridine, %	Yield, ^a %		Ratio of 37/37 or 39/40	
R ₁	R ₂	Sample no.	Time, hr		Monoaddition			
				36 or 39	37 or 40			
CH ₃	Sodium	1	0.5	39	73	27	2.7	
		2	1.0	57	72	28	2.6	
		3	2.0	84	77	23	3.3	
		5	20.5	100	77	23	3.3	
		1	0.5	15	58	42	1.4	
	Potassium	3	1.5	40	57	43	1.3	
		4	2.5	75	56	44	1.3	
		5	6.5	100	57	43	1.3	
		Sodium	1	0.5	23	89	11	8.1
			4	2.0	47	91	9	10.1
5	3.5		60	90	10	9.0		
8	8.0		84	89	11	8.1		
12	12.0		95	90	10	9.0		
Potassium	14	18.0	99 ⁺	90	10	9.0		
	1	0.5	12	90	10	9.0		
	3	1.5	39	88	12	7.3		
	5	3.3	52	85	15	6.7		
	7	7.3	86	87	13	6.7		
CH ₃	C ₂ H ₅	11	12.0	95	86	14	6.1	
		13	15.0	99 ⁺	86	14	6.1	

^a Compounds 36–37 and 39–40 are the products of pentenylation of 4-isopropylpyridine and 4-*sec*-butylpyridine, respectively.

Table V gives the approximate values found for the chemical shifts of the four classes of compounds produced. When diaddition compounds were formed, it was, of course, possible to have two classes present in the same nmr spectrum. Compounds of class I and II gave very predictable spectra. For class I, the

most noticeable peaks are the unsplit methyl peaks, one being *trans* to the side chain and showing resonance at *ca.* δ 1.50 ppm and the other being *cis* to the side chain and giving a resonance peak at *ca.* δ 1.61 ppm. The class II compounds gave an unresolved mass of peaks a δ 0.9–1.9 ppm owing to the saturated side chain.

TABLE IV
 PHYSICAL CONSTANTS FOR PRODUCTS OF ALKENYLATION OF 4-ALKYLPYRIDINES WITH ISOPRENE

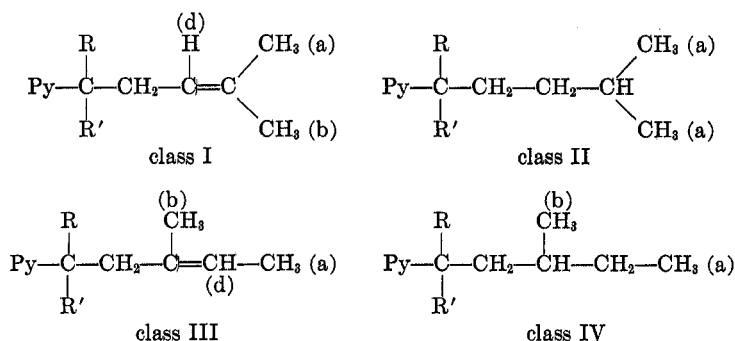
Compd	Bp, °C (mm)	n_D^{20}	Formula	Calcd, %		Found, %		Relative retention times ^a
				C	H	C	H	
1	118-120 (15)	1.5116	C ₁₁ H ₁₅ N	0.46
2	76-77 (2)	1.5122	C ₁₁ H ₁₅ N	81.93	9.38	81.66	9.60	0.50
3 ^b	125-128 (3)	1.5150	C ₁₆ H ₂₃ N	83.79	10.10	84.04	10.14	1.44
4 ^b	125-128 (3)	1.5150	C ₁₆ H ₂₃ N	83.79	10.10	84.04	10.14	1.44
5 ^b	125-128 (3)	1.5150	C ₁₆ H ₂₃ N	83.79	10.10	84.04	10.14	1.44
6	162-165 (3)	1.5257	C ₂₁ H ₃₁ N	2.61
7	162-165 (3)	1.5270	C ₂₁ H ₃₁ N	2.84
8 ^c	162-165 (3)	1.5284	C ₂₁ H ₃₁ N	84.78	10.51	84.61	10.51	3.12
9 ^c	162-165 (3)	1.5286	C ₂₁ H ₃₁ N	3.48
10	78-79 (3.5)	1.4874	C ₁₁ H ₁₇ N	80.92	10.50	80.81	10.80	0.40
11	78-79 (3.5)	1.4907	C ₁₁ H ₁₇ N	80.92	10.50	80.62	10.73	0.42
12 ^b	...	1.4850	C ₁₆ H ₂₇ N	1.02
13 ^b	...	1.4850	C ₁₆ H ₂₇ N	1.02
14 ^b	...	1.4850	C ₁₆ H ₂₇ N	1.02
15	...	1.4858	C ₂₁ H ₃₇ N	83.10	12.29	83.31	12.49	2.05
16	...	1.4979	C ₂₁ H ₃₅ N	83.65	11.70	83.55	11.86	2.60
17 ^d	C ₂₁ H ₃₃ N
18 ^b	85-86 (3)	1.5098	C ₁₂ H ₁₇ N	0.53
19 ^b	85-86 (3)	1.5098	C ₁₂ H ₁₇ N	0.53
20	117-118 (1.5)	1.5213	C ₁₇ H ₂₅ N	1.82
21	117-118 (1.5)	1.5220	C ₁₇ H ₂₅ N	83.89	10.35	83.73	10.53	2.01
22 ^c	130-134 (4)	1.5229	C ₁₇ H ₂₅ N	83.89	10.35	83.91	10.31	2.22
23 ^b	98-100 (8)	1.4877	C ₁₂ H ₁₉ N	81.30	10.80	81.11	10.91	0.43
24 ^b	98-100 (8)	1.4877	C ₁₂ H ₁₉ N	81.30	10.80	81.11	10.91	0.43
25	...	1.4890	C ₁₇ H ₂₅ N	82.53	11.81	82.66	11.84	1.37
26	...	1.5042	C ₁₇ H ₂₇ N	1.75
27 ^b	112-115 (4)	1.5062	C ₁₃ H ₁₉ N	82.48	10.12	82.25	10.25	0.65
28 ^b	112-115 (4)	1.5062	C ₁₃ H ₁₉ N	82.48	10.12	82.25	10.25	0.65
29	146-148 (4)	1.5229	C ₁₈ H ₂₇ N	83.98	10.58	83.77	10.64	2.30
30	146-148 (4)	1.5238	C ₁₈ H ₂₇ N	83.98	10.58	84.09	10.65	2.55
31 ^c	146-148 (4)	1.5243	C ₁₈ H ₂₇ N	83.98	10.58	84.11	10.37	2.76
32 ^b	...	1.4875	C ₁₃ H ₂₁ N	0.53
33 ^b	...	1.4875	C ₁₃ H ₂₁ N	0.53
34	...	1.4902	C ₁₈ H ₃₁ N	1.71
35	...	1.5065	C ₁₈ H ₂₉ N	2.28
36	130-134 (15)	1.5119	C ₁₃ H ₁₉ N	0.67
37	130-134 (15)	1.5132	C ₁₃ H ₁₉ N	82.48	10.12	82.77	10.14	0.74
38	...	1.4917	C ₁₃ H ₂₁ N	81.61	11.07	81.43	11.09	0.56
39	110-112 (3)	1.5133	C ₁₄ H ₂₁ N	82.70	10.41	83.04	10.56	0.92
40	110-112 (3)	1.5144	C ₁₄ H ₂₁ N	82.70	10.41	82.53	10.38	1.05
41	...	1.4938	C ₁₄ H ₂₃ N	0.80

^a Retention times were obtained using a 3.2 m × 0.25 in. column packed with 15% Versamid 900 on 60-80 mesh Gas-Pack WAB. Conditions used were 200° for monoadducts, 225° for diadducts, 245° for triadducts, and a flow rate of 70-75 ml/min. Internal standard was 1,1-diphenylbutane = 1.00 retention time. ^b The compounds within each group were inseparable and the physical constants given are for the mixture. ^c These compounds were isolated from reactions run in a different system; the procedure is given by H. Pines and W. M. Stalick, *Tetrahedron Lett.*, 3723 (1968). ^d This compound was not isolated.

There is an interesting feature in class III compounds due to steric crowding. The spectra of *cis*- or *trans*-3-methyl-2-pentene is quite similar to that described in Table V, as are the spectra of compounds **2**, **4**, **5**, **19**, and **28** (R = H, R' = H, alkyl, alkenyl). However, when examining the spectra of other class III compounds where R and R' are alkyl or alkenyl groups, a noticeable upfield shift is observed for the internal methyl group (b). This methyl group, which has previously been found in the region of δ 1.65 ppm, has now shown a diamagnetic shift to ca. δ 1.15 ppm, or an upfield shift of 0.5 ppm. From examination of space-filling molecular models of these compounds, it becomes clear that, in the compounds where R = H and R' = H, alkyl, or alkenyl, the most stable position for the pentenyl group is away from the pyridine ring. However, for the other compounds in this class (R = R' \neq H), the pentenyl side chain must frequently reside over the

pyridine ring owing to steric crowding. When this occurs, the internal methyl group (b) is much closer to the pyridine ring than is the external methyl group (a). When the methyl group is crowded into the π cloud above the ring, its shielding is increased, since the induced magnetic field of the ring and the applied magnetic fields are opposed.²⁰ Therefore, an upfield shift is noted for the internal methyl group, but virtually no shift is observed for the terminal methyl group. Owing to the hydrogenation procedure used (above), class IV is composed of only five compounds, **11**, **13**, **14**, **24**, and **33**. The spectra show resonance peaks for the terminal methyl group (a) at about δ 0.90 ppm, and for the internal methyl group (b) at about δ 0.94 ppm, but the peaks are not very well resolved from one another.

(20) D. W. Mathieson, "Nuclear Magnetic Resonance for Organic Chemists," Academic Press Inc., New York, N. Y., 1967, p 34.

TABLE V
 NMR DATA FOR GENERAL COMPOUND STRUCTURES


Compd class	Group	δ ppm	Multiplicity
I	a	1.50	Singlet
	b	1.61	Singlet
	d	4.90	Multiplet
II	a	0.85	Doublet
III ^a	a	1.58	Doublet
	b	1.66	Singlet
	d	5.10	Quartet
IV	a	0.90	Triplet
	b	0.94	Doublet

^a See discussion in text about this class of compound.

As was stated earlier, the following compounds were inseparable from one another: **3** and **4** from **5**; **18** from **19**; **27** from **28**; and the hydrogenation products of these compounds. The ratios given in Tables I–III for these compounds were determined by nmr in the following way. A peak at *ca.* δ 1.45 ppm was due to the head-addition isomer, and in the case of compounds **18** and **19** this peak allowed a good approximation of the relative amounts of these two compounds to be made. The ratios of **27/28** and of **3/4/5** were estimated in this same manner, but owing to some overlapping by a peak from the side-chain methylene group the ratios cannot be determined so accurately.

Experimental Section

Reagents.—4-Picoline, 4-ethylpyridine, 4-isopropylpyridine, and 4-*n*-propylpyridine were purchased from Reilly Tar and Chemical Co. The synthesis of 4-*sec*-butylpyridine is described in the following paper.¹⁸ The alkyipyridines were distilled, dried over Linde 5A Molecular Sieves, and then redistilled immediately before use. Ethyl-, *n*-butyl-, and *sec*-butylcyclohexane, used as internal standards for vpc analyses, were obtained by catalytic hydrogenation of the corresponding alkylbenzenes. Isoprene (Aldrich 1-1955-1) was dried over Linde 3A Molecular Sieves and distilled just before use. Analyses by vpc of the above materials indicated them to be of >99.5% purity.

Preparation of Catalyst Solution and General Reaction Procedure.—The equipment used was that described previously.⁸ The catalyst solution was prepared and the reaction procedure was performed as described in previous papers.^{11,12} Dispersion was accomplished at room temperature and the reaction products were separated by distillation. The physical constants of the products thus produced can be found in Table IV.

Catalytic Hydrogenation.—In all cases the mono-, di-, and tripropylated compounds were separated from each other by distillation on a 6-in. Vigreux column. The hydrogenations were carried out by diluting the alkyipyridines with four parts of ethanol and adding 10% of a palladium black catalyst (Englehard, from Sargent No. SC13906) followed by reaction at room tem-

perature and atmospheric pressure. The reaction mixture was checked by vpc, and, when *ca.* 95% of the tail-addition product was hydrogenated, the reaction was quenched. This allowed the selective hydrogenation of the tail-addition product with little or no hydrogenation of the head-addition product. The ethanol was evaporated under a stream of nitrogen and the products were separated by vpc.

Analysis of Products.—The infrared spectra of the pure samples were taken with a Baird Model 4-55 spectrophotometer calibrated at 5.14 μ with a polystyrene film. The nmr spectra were taken with a Varian Model A-60 nmr spectrophotometer using tetramethylsilane as an internal standard. Microanalyses were performed by either MicroTech Laboratories, Skokie, Ill., or M-H-W Laboratories, Garden City, Mich. Vapor phase chromatographic analysis and separations were performed on a F & M Model 720 dual-column instrument equipped with a thermal-conductivity detector and using helium as a carrier gas. The separations and identifications of the various alkenylated pyridines were accomplished with various columns with diameters of $1/8$ – $3/8$ in. and lengths of 2.3–16.1 m, packed with 5–15% Versamide 900 on 60–100 mesh Gas Pack WAB.

Registry No.—**1**, 22253-14-1; **2**, 22253-15-2; **3**, 22253-16-3; **4**, 22253-17-4; **5**, 22253-18-5; **6**, 22297-86-5; **7**, 22253-19-6; **8**, 22253-20-9; **9**, 22297-87-6; **10**, 22241-38-9; **11**, 22241-39-0; **12**, 22253-23-2; **13**, 22253-24-3; **14**, 22253-25-4; **15**, 22253-26-3; **16**, 22253-27-6; **18**, 22253-28-7; **19**, 22253-29-8; **20**, 22253-30-1; **21**, 22253-31-2; **22**, 22253-32-3; **23**, 22253-33-4; **24**, 22253-34-5; **25**, 22253-35-6; **26**, 22253-36-7; **27**, 22253-37-8; **28**, 22253-38-9; **29**, 22297-88-7; **30**, 22253-39-0; **31**, 22253-40-3; **32**, 22241-55-0; **33**, 22241-56-1; **34**, 22241-57-2; **35**, 22241-58-3; **36**, 22241-59-4; **37**, 22241-60-7; **38**, 22241-61-8; **39**, 22241-62-9; **40**, 22241-63-0; **41**, 22241-64-1; isoprene, 78-79-5.

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