gen. The dark brown reaction mixture was then cooled and transferred to a 100-ml capacity Magne-Dash autoclave with an agitator. After this was flushed with nitrogen, 40 atm of ethylene was introduced and the autoclave was heated at 208° until the uptake of ethylene ceased. The sodium was then decomposed with ethanol and the reaction product was dissolved in ether, washed, dried ($MgSO_4$), and distilled. Title compound **11** distilled at 125–128° (1–1.5 mm) and was purified by preparative vpc: $n^{20}D$ 1.5640. *Anal.* Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.98; H, 10.28. The synthetic sample was identical with the isolated product **14** (expt 10 and 11, Table III).

Registry No.—Ethylene, 74-85-1; **2**, 2765-18-6; **3**, 3042-56-6; **4**, 19990-00-2; **6**, 19990-01-3; **8**, 2027-19-2; **9**, 3042-57-7; **10**, 19990-03-5; **11**, 17057-92-0; **12**, 479-58-3; **13**, 19990-06-8; **14**, 19990-07-9; **15**, 19990-08-0; **17**, 4944-94-9; **18**, 232-54-2; **24**, 6619-57-4.

Base-Catalyzed Reactions. XXXIV.[1] The Alkali Metal Catalyzed Side-Chain Aralkylation of 2- and 4-Alkylpyridines with Styrene, α-Methylstyrene, and *cis*- and *trans*-β-Methylstyrene

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The sodium- and potassium-catalyzed side-chain aralkylation reactions of 2- and 4-alkylpyridines with styrene, α-methylstyrene, and *cis*- and *trans*-β-methylstyrene were performed using the alkylpyridines in a 5:1 molar excess. For the most part, the reactions proceed readily at 0–25° to yield monoaddition products *via* a Michael-type addition mechanism, as well as di- and triaddition products in some cases. As the length and branching of the alkylpyridine are increased, the yields of the higher adducts decrease. The yields of the higher adducts, as well as the relative rates of reaction, also decrease as the steric hindrance of the reacting olefin increases on going from styrene to α-methylstyrene to β-methylstyrene. 4-Alkylpyridines react more readily than 2-alkylpyridines. Also formed, in some cases, are diaddition products resulting from a chain-lengthening process. With 2- and 4-picoline and 2- and 4-ethylpyridine, *trans*-β-methylstyrene reacts faster than *cis*, due to the greater conjugation of the *trans* olefin. With 4-isopropylpyridine, however, the results are reversed.

The sodium- and potassium-catalyzed side-chain aralkylations of alkylbenzenes having a benzylic hydrogen have been studied extensively in our laboratory.[3] These reactions proceed in the presence of a promoter at 100–125° to give the expected monoaddition products, and diadducts in some cases, *via* a carbanion mechanism. As the length and branching of the alkylbenzene is increased, and as the steric hindrance of the olefin increases on going from styrene to α-methylstyrene to β-methylstyrene, the yields of the aralkylation products decrease while the competitive dimerization and polymerization of the olefin increases.[4] The potassium-catalyzed aralkylation of *n*-alkylbenzenes with β-methylstyrene at 105° gives only fair yields (19–52%) of the monoaddition products, while isopropylbenzene fails to react with β-methylstyrene. Instead, the β-methylstyrene undergoes dimerization by both anionic and anionic free-radical mechanisms.[5,6]

It has been reported that alkylpyridines can undergo alkali metal catalyzed side-chain alkylation reactions similar to the side-chain alkylations of alkylbenzenes.[3,7] The sodium- and potassium-catalyzed aralkylation reactions of 2- and 4-alkylpyridines with styrene, α-methylstyrene, and *cis*- and *trans*-β-methylstyrene were studied in order to compare the results with those of the analogous reactions with alkylbenzenes.

Discussion of Results

The reactions of 2- and 4-alkylpyridine with styrene, α-methylstyrene, and *cis*- and *trans*-β-methylstyrene were carried out in the presence of catalytic amounts of sodium and potassium. Details and results of the aralkylations are given in Tables I and II. The course of the reactions was followed by vapor phase chromatography. The products were separated by preparative gas chromatography and their structures were established by nmr and ir spectroscopy, elemental analyses, and occasionally by comparison with known compounds.

The metallic sodium or potassium was dispersed in the alkylpyridine for 3–5 hr to ensure complete dispersion, resulting in the formation of a seemingly homogeneous solution of organoalkali metal catalyst, R^-M^+. The olefin was then added dropwise. For the most part the reactions proceed readily at 0–25°.

The mechanism of the aralkylation is proposed to be similar to that of the side-chain aralkylation of alkylbenzenes[8] and the side-chain alkenylation of 4-alkylpyridines.[7d] The initial step is suspected to be the formation of a radical anion.[1]

The aralkylation reaction can be described by the following equation. If R_1 and/or R_2 = H, further aralkylation of the alkylpyridine does occur, resulting in the formation of normal di- and triadducts. The diaddition products can also be formed to a smaller extend *via* a chain-lengthening process similar to that which has previously been reported.[8,9]

In Table I are listed the results of the reactions of various alkylpyridines with styrene and α-methylstyrene. As the length and branching of the alkylpyri-

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[1] (a) Paper XXXIII: B. Stipanovic and H. Pines, *J. Org. Chem.*, **34**, 2106 (1969); (b) paper V of the series Alkylation of Heteroaromatics.

[2] Predoctoral Fellow, National Institutes of Health, 1964–1968.

[3] For literature references, see H. Pines and L. Schaap, *Advan. Catalysis*, **12**, 116 (1960).

[4] J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

[5] J. Shabtai, E. M. Lewicki, and H. Pines, *ibid.*, **27**, 2618 (1962).

[6] J. Shabtai and H. Pines, *ibid.*, **29**, 2408 (1964).

[7] (a) H. Pines and D. Wunderlich, *J. Amer. Chem. Soc.*, **81**, 2568 (1959); (b) H. Pines and B. Notari, *ibid.*, **82**, 2209 (1960); (c) *ibid.*, **82**, 2945 (1960); (d) H. Pines and J. Oszczapowicz, *J. Org. Chem.*, **32**, 3183 (1967).

[8] H. Pines and D. Wunderlich, *J. Amer. Chem. Soc.*, **80**, 6001 (1958).

[9] H. Pines and N. Sih, *J. Org. Chem.*, **30**, 280 (1965).

TABLE I

ALKALI METAL CATALYZED SIDE-CHAIN ARALKYLATION OF 4-ALKYLPYRIDINES WITH STYRENE

Expt	4-Alkyl	Mole	Styrene, mole	Catalyst	g[a]	Temp, °C	Intern. std[b]	Product distribn,[c] % Mono-adduct	Diad-duct	Triad-duct	Other
1	CH_3	0.375	0.075	Na	0.30	0	A	41.1	41.8	12.7	4.4
2		0.375	0.075	K	0.30	0	A	40.0	40.9	16.0	3.1
3	CH_2CH_3	0.375	0.075	Na	0.30	0	A	83.0[d]	17.0	Trace	
4		0.190	0.038	K	0.15	0	A	89.2[d]	10.8	Trace	
5	$CH_2CH_2CH_3$	0.20	0.04	Na	0.20	0	D	76.0	24.0		
6	$CH(CH_3)_2$	0.190	0.038	Na	0.15	0	B	74.9	25.1[e]		
7		0.190	0.038	K	0.15	0	B	74.3	25.7[e]		
			α-Methylstyrene, mole								
8	CH_3	0.375	0.075	Na	0.30	0	A	65.1	26.8[e]		8.1
9		0.375	0.075	K	0.30	0	A	55.2	35.2[e]		9.6
10	CH_2CH_3	0.190	0.038	Na	0.15	0	A	76.6[d]	21.4[e]		2.1
11		0.375	0.075	K	0.30	0	A	84.7[d]	13.3[e]		2.0
12	$CH(CH_3)_2$	0.175	0.035	Na	0.15	0	B	85.7	14.3[b,f]		
13		0.175	0.035	K	0.15	0	B	85.4	14.6[b,f]		
			β-Methylstyrene,[g] mole								
14	CH_3	0.125	0.025	Na	0.10	0	C	98.0			2.0
15		0.125	0.025	K	0.10	0	C	99.0			1.0
16	CH_2CH_3	0.190	0.038	Na	0.15	0	B	96.9			3.1
17		0.190	0.038	K	0.15	0	B	99.0			1.0
18	$CH(CH_3)_2$	0.140	0.028	Na	0.10	25	B	93.0			7.0
19		0.140	0.028	K	0.10	25	B	94.0			6.0
20		0.050	0.010	K	0.05	75	B	92.5			7.5

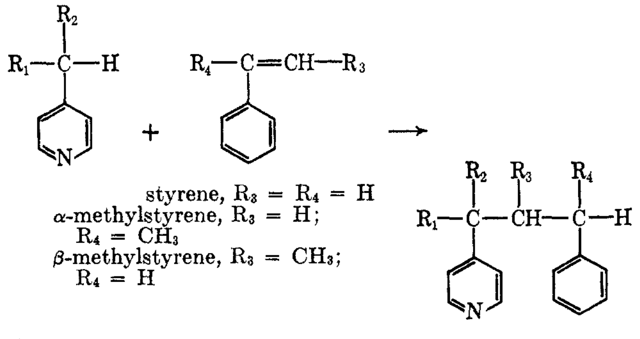
[a] Weight of catalyst is approximate. [b] Amount of internal standard used = 0.01 mole. A = *sec*-butylcyclohexane, B = ethylcyclohexane, C = *n*-butylcyclohexane. [c] Percentages were based on vpc peak area, uncorrected by thermal conductivity factors, calculated by triangulation method after 100% reaction of α-methylstyrene. [d] Monoadduct consisted of two compounds, a pair of diastereoisomers, resolvable by vapor phase chormatography. [e] Product actually a mixture of stereoisomers, unresolvable by vapor phase chromatography. [f] Diadduct suspected to be 2,4-dimethyl-4,6-diphenyl-2-(4-pyridyl)heptane, produced *via* a chain-lengthening process. [g] β-Methylstyrene used was a mixture of 81% *trans*-, 17.5% *cis*-, and 1.5% allylbenzene.

TABLE II

SODIUM-CATALYZED SIDE-CHAIN ARALKYLATION OF 2-ALKYLPYRIDINES WITH *cis*- AND *trans*-β-METHYLSTYRENE

Expt	2-Alkyl	Mole	Styrene, mole	Na, g[a]	Temp, °C	Intern. std[c]	Products, %[d] Mono-adduct	Diad-duct	Others
21	CH_3	1.00	0.20	1.0	25	A	69.0	26.0	5.0[h]
			β-Methylstyrene,[b] mole						
22	CH_3	0.125	0.025	0.15	55	D	>99		
23	CH_2CH_3	0.125	0.025	0.15	55	D	>99		≃72[f,g]
24	$CH(CH_3)_2$	0.10	0.020	0.10	115	B	0[e]		≃72[f,g]

[a] Weight of catalyst is approximate. [b] β-Methylstyrene used was a mixture of 81% *trans*-, 17.5% *cis*-, and 1.5% allylbenzene. [c] Amount of internal standard used = 0.01 mole. A = *sec*-butylcyclohexane, B = ethylcyclohexane, D = isopropylcyclohexane. [d] Percentages were based on vpc peak areas, uncorrected by thermal conductivity factors, calculated by triangulation method after 100% reaction of β-methylstyrene. [e] No aralkylation reaction occurred; instead, both the β-methylstyrene and 2-isopropylpyridine underwent self-condensation reactions. [f] Product shown to be a dimer of β-methylstyrene, *i.e.*, *trans*-4-methyl-1,5-diphenyl-1-pentene (17). [g] Remainder of β-methylstyrene underwent further reaction to polymeric products. [h] Triadduct.



dine increases the relative rate of the reaction decreases, as do the amounts of the higher adducts. Little difference is noticed between sodium and potassium as catalysts.

Even though the molar ratio of 4-picoline to styrene was 5:1, both di- and triaddition products were found. This indicates that the secondary carbanion of the monoadduct, once formed, reacts faster than 4-picoline carbanion with the remaining styrene. Similar observations have been made in the reaction of alkylbenzenes with styrene[8] and in the ethylation[7c] and competitive alkenylation of 4-alkylpyridines.[10] Also, in the Michael addition of unsymmetrical ketones to α,β-unsaturated carbonyl compounds, reaction occurs largely at the more highly substituted α carbon of the unsymmetrical ketone.[11]

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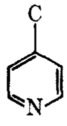
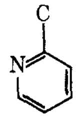
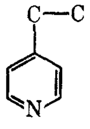
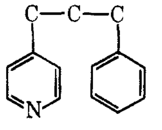
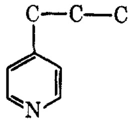
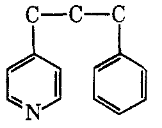
(10) H. Pines and W. M. Stalick, unpublished results.

(11) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 208-210.

TABLE III

COMPETITIVE SODIUM-CATALYZED SIDE-CHAIN ARALKYLATION OF ALKYLPYRIDINES WITH STYRENE

Expt	Alkylpyridines used X	Y	Molar ratio[a] X:Y:styrene	Temp, °C	Intern. std[b]	Molar ratio of monoadducts[c] X:Y
25			10:10:1	0	A	99:1[d]
26			10:10:1	0	A	1:1
27			10:10:1	0	D	1:2.5

[a] 0.20 mol of alkylpyridine and 0.1 g of sodium were used. [b] Amount of internal standard used = 0.01 mol. A = *sec*-butylcyclohexane, D = isopropylcyclohexane. [c] Percentages corrected by thermal conductivity factors. [d] Also formed is small amount of diadduct from X.

In the reactions of both 4-ethylpyridine and 4-*n*-propylpyridine with styrene, the diaddition product consisted of two compounds formed in roughly equal amounts, unresolvable by preparative gas chromatography, one of which in each case results from a normal diaddition process and the other from a chain-lengthening diaddition. In a similar reaction, Chumakov and Ledovskikh reported only the normal diaddition product.[12]

In Tables I and II, expt 14–24, are given the results of the reactions of alkylpyridines with *cis*- and *trans*-β-methylstyrene. The reactions of β-methylstyrene are much slower than the corresponding reactions of styrene and α-methylstyrene, presumably because of a more pronounced steric effect with a β-methyl as compared to an α-methyl substituent in the styrene molecule.[5,13] These increased steric factors are also responsible for the almost exclusive formation of monoaddition products.

In the reactions of 2- and 4-picoline and 2- and 4-ethylpyridine with a mixture of *cis*- and *trans*-β-methylstyrene, *trans*-β-methylstyrene was detected by vpc to react much faster than *cis*. These kinetic differences between *cis*- and *trans*-β-methylstyrene probably are related to a difference in the conjugation of the double bond with the ring in the two compounds. Molecular models indicate that steric hindrance exists between the methyl group and the *o*-hydrogen of the phenyl ring in the *cis* compound. This prevents complete conjugation of the π-electron orbitals of the double bond and the ring by restricting coplanarity.[13,14] In the *trans* compound no such internal interactions are present. That *trans*-β-methylstyrene is more conjugated than the *cis* is reflected in the ultraviolet spectra.[15]

In the reaction of 4-isopropylpyridine and *cis*- and *trans*-β-methylstyrene, however, the results are reversed and the *cis* compound reacts faster. To explain these results it is necessary to assume that change in the rate-determining step must take place due to the increased steric requirements of 4-isopropylpyridine. The possibility also exists that only *trans*-β-methylstyrene undergoes the aralkylation reaction and that *cis–trans* isomerization is occurring.

An unsuccessful attempt was made to treat β-methylstyrenes with 2-isopropylpyridine below 100°. As the temperature was increased to 115°, the β-methylstyrene underwent an anionic dimerization reaction leading to *trans*-1,5-diphenyl-4-methyl-1-pentene (**17**),[6] and the reaction was further complicated by self-condensation reactions of two molecules of 2-isopropylpyridine.

In an effort to confirm the greater reactivity of 4-alkylpyridines *vs.* 2-alkylpyridines,[7c] a competitive sodium-catalyzed reaction was carried out between 2- and 4-picoline with styrene (Table III). The monoadduct of 4-picoline was formed almost exclusively. Also performed were competitive reactions with styrene of 4-ethylpyridine and 4-*n*-propylpyridine, respectively, with 1-phenyl-3-(4-pyridyl)propane. The relative rate of aralkylation of 4-ethylpyridine as compared to 1-phenyl-3-(4-pyridyl)propane was about 1:1, while 4-*n*-propylpyridine reacts slower than 1-phenyl-3-(4-pyridyl) propane by a relative ratio of 1:2.5. The relative reaction rate of 4-ethylpyridine *vs.* 4-*n*-propylpyridine is then calculated to be 2.5:1. This ratio is consistent with the figures of 1.9:1 and 2.5:1 obtained in the competitive ethylation[7c] and alkenylation,[10] respectively, of these two alkylpyridines.

Of particular note is that 1-phenyl-3-(4-pyridyl)propane reacts 2.5 times faster than 4-*n*-propylpyridine, although steric factors are apparently greater in the former. In an analogous situation, it was found that the butenylation of 1-(4-pyridyl)-3-pentene occurred 4.5 times faster than 4-*n*-propylpyridine.[7d] This difference in the rates of alkenylation was explained in terms of the greater acidity of 1-(4-pyridyl)-3-pentene, due to π-electron bonding of the picolyl hydrogen with the double bond of the alkenyl group. A somewhat similar situation may exist with 1-phenyl-3-(4-pyridyl)-propane, where the phenyl ring assists in the removal of

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

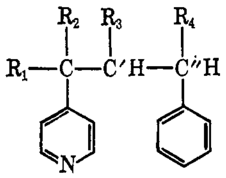
[13] D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3883 (1948).

[14] G. Favini and M. Simonetta, *Theoret. Chim. Acta*, **1**, 294, (1963).

[15] C. G. Overberger, D. Tamer, and E. M. Pearce, *J. Amer. Chem. Soc.* **80**, 4566 (1958).

TABLE IV

CHEMICAL SHIFTS IN NMR SPECTRA OF PRODUCTS OF CLASS I[a]



Compd[c]	C	C′H	C″H	R₁	R₂	R₃	R₄
	δ, ppm[b]						
1, R_1–R_4 = H	2.50 (2) m	1.94 (2) m	2.50 (2) m				
2, R_1 = CH_2CH_2Ph; R_2–R_4 = H	2.28 (1) m	1.85 (4) m	2.28 (4) m				
3, R_1 = R_2 = CH_2CH_2Ph; R_3 = R_4 = H		1.90 (6) m	2.22 (6) m				
4, R_1 = CH_3; R_2–R_4 = H	2.56 (1) m	1.90 (2) m	2.56 (2) m	1.22 (3) d (*J* = 6.8)			
5, R_1 = R_2 = CH_3; R_2 = R_4 = H		1.82 (2) m	2.26 (2) m	1.29 (3) s	1.29 (3) s		
6,[g] R_1 = R_2 = CH_3; R_3 = H; R_4 = CH_2CH_2Ph		1.90 (2) m	2.40 (1) m	1.14 (3) s	1.02 (3) s		1.90 (2) m, 2.20 (2) m
7, R_1–R_3 = H; R_4 = CH_3	2.40 (2) m	1.85 (2) m	2.58 (1) m				1.22 (3) d (*J* = 6.8)
8,[i] R_1 = $CH_2CHPhCH_3$; R_2 = R_3 = H; R_4 = CH_3	2.35 (1) m	1.95 (4) m	2.35 (2) m				0.90–1.30 (6) m
9A,[k] R_1 = R_4 = CH_3; R_2 = R_3 = H	2.40 (1) m	1.85 (2) m	2.40 (1) m	1.16 (3) d (*J* = 6.8)			1.16 (3) d (*J* = 6.8)
9B,[k] R_1 = R_4 = CH_3; R_2 = R_3 = H	2.50 (1) m	1.82 (2) m	2.50 (1) m	1.18 (3) d (*J* = 6.8)			1.20 (3) d (*J* = 6.8)
10,[j] R_1 = $CH_2CHPhCH_3$; R_2 = R_4 = CH_3; R_3 = H		1.95 (4) m	2.40 (2) m		0.85–1.30 (3) m		0.85–1.30 (6) m
11,[h] R_1 = R_2 = R_4 = CH_3; R_3 = H		1.97 (2) m	2.45 (1) m	1.21 (3) m	1.10 (3) s		1.06 (3) d (*J* = 6.0)
12, R_1 = R_2 = R_4 = H; R_3 = CH_3	2.47 (2) m	2.10 (1) m	2.47 (2) m			(*J* 6.0)	
13,[e] R_1 = R_3 = CH_3; R_2 = R_4 = H	2.60 (1) m	2.00 (1) m	2.45 (2) m	1.24 (3) d (*J* = 7.0)		0.72 (3) d[d] (*J* = 7.5)	
14,[f] R_1–R_3 = CH_3; R_4 = H		2.60 (1) m	2.15 (2) m	1.34 (3) s	1.29 (3) s	0.70 (3) d[d] (*J* = 6.0)	
18, R_1 = CH_2CH_3; R_2–R_4 = H	2.32 (2) m	1.90 (2) m	2.32 (2) m	1.80 (2) m, 0.73 (3) t (*J* = 7.0)			

[a] All products in this class result from addition of styrene, α-methylstyrene, or β-methylstyrene to 4-alkylpyridines. Their spectra therefore show two α-hydrogens and two β-hydrogens of an α-substituted pyridine ring in the regions 8.3–8.7 and 6.7–7.1 ppm, respectively, and phenyl hydrogens of monosubstituted phenyl rings in the region 6.9–7.3 ppm.

[b] Numbers in parentheses refer to integrated number of protons: s = singlet, d = doublet, t = triplet, m = multiplet. *J* values are given cycles per second.

[c] Refer to Table VII for compound names.

[d] Actually two sets of doublets due to asymmetric center.

[e] Contain two asymmetric carbon atoms, therefore two stereoisomers are present. The enantiomers were not resolvable by vpc and as a result the nmr is that of a mixture of both stereoisomers. Both methyl groups are in different magnetic environment and they appear as two doublets. This type of spectral patterns has been previously reported: J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice Hall, Inc., Englewood Cliffs, N. J., 1965, pp 119–122: P. M. Nair and J. D. Roberts, *J. Amer. Chem. Soc.*, **79**, 4565 (1957); J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 58–60.

[f] Contains one asymmetric carbon atom. Therefore, the two methyl groups, R_1 and R_2, although seemingly identical, appear as two singlets as a result of the molecular asymmetry.

[g] Diadduct formed *via* a chain lengthening. The nmr situation is similar to that of footnote *f*.

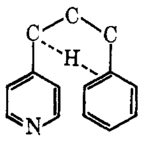
[h] The two methyl groups, R_1 and R_2, appear as two singlets at 1.10 and 1.21 ppm, the former overlapping one peak of the doublet of the other methyl group centered at 1.06 ppm.

[i] The following stereoisomers exist in **8** (E. L. Eliel, "Stereochemistry, of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 28): *R*, *R* (enantiomer), *S*, *R R* (enantiomer), (2*), *S* (*meso*), *R* (S*), *S* (*meso*). These isomers were unresolvable by vpc, and therefore the nmr is that of a mixture of the above stereoisomers. As a result, the methyl groups, being magnetically nonequivalent in the various stereoisomers, appear as a series of peaks integrating to the expected six hydrogens in the region from 0.90 to 1.30 ppm.

[j] This compound presents a situation similar to **8** (footnote *i*), but the methyl, R_2, further complicates the nmr in this region. The three methyl groups integrate to the expected nine hydrogens.

[k] Compounds **9A** and **9B** are enantiomers, formed in a ratio of 2:3, and were resolved by preparative gas chromatography (column H).

this hydrogen by the π-electron bonding postulated, although in this case the π-electron system is one carbon further removed.

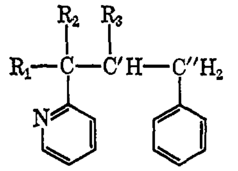


An alternative explanation for the apparent greater reactivity of 1-phenyl-3-(4-pyridyl)propane can be postulated in terms of the stability of the resultant carbanion, by assuming π-electron overlap of the two aromatic rings involved. The negative charge on the α carbon of the pyridine ring is therefore partially delocalized over both rings as opposed to only one in 4-*n*-propylpyridine. Molecular models indicate that such overlap is sterically favorable.

Structure Determination.—The primary tool for structure determination of the products was nmr. The ir spectra were all consistent with the proposed structures and will not be discussed except where

TABLE V

CHEMICAL SHIFTS IN NMR SPECTRA OF PRODUCTS OF CLASS II[a]



Compd[c]	δ, ppm[b]: C	C′H	C″H₂	R₁	R₃
15, $R_1 = R_2 = H$; $R_3 = CH_3$	2.55 (2) m	2.35 (1) m	2.55 (2) m		0.82 (3) d (J = 5.5)
16,[c] $R_1 = R_3 = CH_3$; $R_2 = H$	2.75 (1) m	2.15 (1) m	2.75 (2) m	1.32 (3) d[e] (J = 7.0)	0.75 (3) d[d] (J = 6.0)
19, R_1–R_3 = H	2.68 (2) m	2.08 (2) m	2.68 (2)m		
20, $R_1 = CH_2CH_2Ph$; $R_2 = R_3 = H$	2.55 (1) m	2.04 (4) m	2.44 (4) m		
21, $R_1 = R_2 = CH_2CH_2Ph$; $R_3 = H$		1.96 (6) m	2.34 (6) m		

[a] All products in this class result from addition of 2-alkylpyridine to styrene or β-methylstyrene. Their spectra therefore show one α-, and γ-, and two β-hydrogens of an α-substituted pyridine ring in the regions 8.4–8.5, 7.3–7.4, and 6.8–7.0, respectively, and phenyl hydrogens from monosubstituted phenyl rings in the region 6.9–7.2 ppm. [b–e] See corresponding footnotes in Table IV.

TABLE VI

VAPOR PHASE CHROMATOGRAPHIC DETAILS OF ARALKYLATION REACTIONS

Expt[a]	Products[b]	Vpc column[c]	Programming rate, °C/min	Temp limits, °C	Column[d]	Temp, °C
2	**1–3**	A	13	100–290	D[e]	280
3, 4	**4**[f]	A	13	90–290	D	210
6, 7	**5, 6**	A	13	100–290	D	240
8, 9	**7, 8**	A	13	100–290	D	260
10, 11	**9A, 9B, 10**	A	13	80–290	D[g]	240
12, 13	**11**[h]	A	13	100–290	B	270
14, 15	**12**	A	13	85–280	D	180
16, 17	**13**	A	9	85–275	C	200
18–20	**14**	F	15	100–235	B	230
22	**15**	A	9	70–275	C	200
23	**16**	A	9	75–275	B	230
24	**17**[i]	G	9	70–275	K	235
5	**18**[j]	G	9	90–275	D	230
21	**19–21**	G	9	80–280	D[e]	270
25	**1, 19**[k]	G	9	80–275		
26	**2, 4**[k]	G	6.4	70–275		
27	**2, 18**[k]	A	9	90–275		

[a] Refer to Tables I–III for reactants. [b] Refer to Table VII. [c] Chromatographic column was used to follow progress of reaction. [d] Preparative chromatographic column was used to separate products. [e] Compounds **3** and **21** were recycled on column E at 270°. [f] Two diaddition products, unresolvable by preparative gas chromatography, are also produced, presumably 3-methyl-1,5-diphenyl-3-(4-pyridyl)pentane and 1,3-diphenyl-5-(4-pyridyl)hexane. [g] Compounds **9A** and **9B** were collected together and then separated on column H at 200°. [h] A diaddition product, believed to be 2,4-dimethyl-4,6-diphenyl-2-(4-pyridyl)heptane, was also produced. [i] Self-condensation products of 2-isopropylpyridine were not isolated. [j] Two diaddition products unresolvable by preparative gas chromatography, are also produced, presumably 3-ethyl-1,5-diphenyl-3-(4-pyridyl)pentane and 1,3-diphenyl-5-(4-pyridyl)heptane. [k] Products identified by comparison of their relative retention times on columns F and G with previously identified compounds.

particularly pertinent. For the most part, the nmr spectra are quite explicit for the proposed structures and can be divided into two general classes, Tables IV and V. Asymmetric centers were generated in the formation of many products. As a result, their nmr spectra show significant characteristics arising from the molecular nonequivalence caused by the molecular asymmetry.

Not belonging to either class I or II the dimerization product of β-methylstyrene, *trans*-4-methyl-1,5-diphenyl-1-pentene (**17**), formed in the reaction of 2-isopropylpyridine with β-methylstyrene. This compound was identified by its similar relative retention time on columns F, G, and I with a known sample available in our laboratory. It was further characterized by nmr, which shows ten phenyl hydrogens of two different monosubstituted phenyl rings at 7.13 and 7.20 ppm. Two vinyl hydrogens are centered at 6.20 ppm, while the two benzylic methylene hydrogens are centered at 2.52 ppm. The two allylic methylene hydrogens and the methine hydrogen overlap in the region 1.80–2.30 ppm. The methyl group appears as a doublet (J = 6.0 cps) centered at 0.90 ppm. The strong band at 10.41 μ in the infrared spectrum indicates the olefin is *trans*.

Experimental Section

Reagents.—2- and 4-picoline, 2- and 4-ethylpyridine, 4-*n*-propylpyridine, and 4-isopropylpyridine were obtained from Reilly Tar and Chemical Co. They were distilled and dried over Linde 13X Molecular Sieves before use. Isopropylpyridine was synthesized.[16]

Internal standards, ethylcyclohexane, isopropylcyclohexane,

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

TABLE VII
PHYSICAL CONSTANTS AND ELEMENTAL ANALYSES OF REACTION PRODUCTS

			Calcd, %			Found, %			
No.	Compound	Formula	C	H	N	C	H	N	n^{22}_{D} (lit.[8] n^{20}_{D})
1	1-Phenyl-3-(4-pyridyl)propane	$C_{14}H_{15}N$	85.24	7.66	7.10	85.06	7.54	7.06	1.5604 (1.5620)
2	1,5-Diphenyl-3-(4-pyridyl)pentane	$C_{22}H_{23}N$	87.66	7.69	4.65	87.80	7.77	4.63	1.5809 (1.5810)
3	1,5-Diphenyl-3-(2-phenylethyl)-3-(4-pyridyl)pentane	$C_{30}H_{31}N$	88.84	7.71	3.45	88.59	7.77	3.57	1.5875
4	1-Phenyl-3-(4-pyridyl)butane	$C_{15}H_{17}N$	85.26	8.11	6.63	85.13	8.16	6.68	1.5543 (1.5545)
5	3-Methyl-1-phenyl-3-(4-pyridyl)butane	$C_{16}H_{19}N$	85.28	8.50	6.22	85.49	8.60	6.12	1.5522
6	5-Methyl-1,3-diphenyl-5-(4-pyridyl)hexane	$C_{24}H_{27}N$	87.50	8.25	4.25	87.29	8.17	4.08	1.5732
7	3-Phenyl-1-(4-pyridyl)butane	$C_{15}H_{17}N$	85.26	8.11	6.63	85.21	8.17	6.54	1.5543
8	2,6-Diphenyl-4-(4-pyridyl)heptane	$C_{24}H_{27}N$	87.50	8.25	4.25	87.57	8.46	4.08	1.5763
9A	2-Phenyl-4-(4-pyridyl)pentane	$C_{16}H_{19}N$	85.28	8.50	6.22	85.40	8.56	6.12	1.5456
9B	2-Phenyl-4-(4-pyridyl)pentane	$C_{16}H_{19}N$	85.28	8.50	6.22	85.45	8.52	6.15	1.5471
10	4-Methyl-2,6-diphenyl-4-(4-pyridyl)heptane	$C_{25}H_{29}N$	87.41	8.51	4.08	87.48	8.66	4.03	1.5710
11	2-Methyl-4-phenyl-2-(4-pyridyl)pentane	$C_{17}H_{21}N$	85.31	8.84	5.85	85.59	8.84	5.72	1.5485
12	2-Methyl-1-phenyl-3-(4-pyridyl)propane	$C_{15}H_{17}N$	85.26	8.11	6.63	84.97	8.20	6.54	1.5545
13	2-Methyl-1-phenyl-3-(4-pyridyl)butane	$C_{16}H_{19}N$	85.28	8.50	6.22	85.16	8.59	6.14	1.5536
14	2,3-Dimethyl-1-phenyl-3-(4-pyridyl)butane	$C_{17}H_{21}N$	85.31	8.84	5.85	85.21	8.76	5.69	1.5560
15	2-Methyl-1-phenyl-3-(2-pyridyl)propane	$C_{15}H_{17}N$	85.26	8.11	6.63	85.16	8.11	6.75	1.5533
16	2-Methyl-1-phenyl-3-(2-pyridyl)butane	$C_{16}H_{19}N$	85.28	8.50	6.22	85.15	8.57	6.32	1.5518
17	*trans*-4-Methyl-1,5-diphenyl-1-pentene	$C_{18}H_{20}$	91.47	8.53		91.48	8.43		1.5728 (lit.[6] 1.5710)
18	1-Phenyl-3-(4-pyridyl)pentane	$C_{16}H_{19}N$	85.28	8.50	6.22	85.40	8.60	6.27	1.5507
19	1-Phenyl-3-(2-pyridyl)propane	$C_{14}H_{15}N$	85.24	7.66	7.10	85.25	7.85	7.23	1.5610 (1.5585)
20	1,5-Diphenyl-3-(2-pyridyl)pentane	$C_{22}H_{23}N$	87.66	7.69	4.65	87.95	7.85	4.50	1.5796 (1.5773)
21	1.5-Diphenyl-3-(2-phenylethyl)-3-(2-pyridyl)pentane	$C_{30}H_{31}N$	88.84	7.71	3.45	88.62	7.98	3.37	1.5874

n-butylcyclohexane, and *sec*-butylcyclohexane, were obtained by hydrogenation of the corresponding alkylbenzenes. *cis*- and *trans*-β-methylstyrene were obtained by dehydration of phenylethylcarbinol over alumina. The olefins consisted of 73% *trans* and 23% *cis* isomers and 3% of allylbenzene. Pure *cis*- and *trans*-β-methylstyrene were separated by preparative gas chromatography on column J (see below) at 120°. All reagents were at least 99.5% pure, adjudged by vpc.

General Procedure for Aralkylation Reactions.—The catalyst was prepared by dispersion of freshly cut alklai metal in the alkylpyridine for 3–5 hr to ensure complete dispersion. The reactions were performed under a slow stream of dry N_2 on a three-necked flask equipped with reflux condenser and a self-sealing rubber septum. The active catalyst was a brown-black solution, seemingly homogeneous. An inert nonaromatic hydrocarbon was added as internal standard, followed by the slow addition of reacting olefin by syringe at the reaction temperature. During the reaction samples were withdrawn periodically, decomposed with methanol, and analyzed by vpc. At the conclusion of the reaction, the catalyst was decomposed with methanol at 0°. The reaction mixture was then taken up in ether and washed with water. The organic layer was dried over $MgSO_4$ and then distilled under reduced pressure to remove excess methanol, alkylpyridine, and internal standard. The products, contained in the residue, were then separated and collected by preparative gas chromatography.

Vapor Phase Chromatography (Table VI).—F & M Model 300 programmed-temperature gas chromatograph was used for analytical determination, while aerograph Model A-700 chromatograph was employed for separation of reaction products. Helium was used as a carrier gas with a rate of 85–90 ml/min. The progress of all reactions was followed.

Description of Columns.—**Substrates** for the columns were 15% silicone gum rubber SE-30 (A–F), 10% (G), 15% Versamid 600 (F, K), 10% (H), 15% Carbowax 20M (I, J).

Solid supports for the columns were Gas Pack WAB 60–80 mesh (A–G), 60–100 mesh (K), Gas Pack W 80–100 mesh (H), Chromosorb P 30–60 mesh (I, J).

Dimension of copper tubings were 0.75 ft × $^3/_8$ in. (E), 1.5 ft × $^3/_8$ in. (D), 3 ft × $^1/_8$ in. (C), 5 ×0.25 in. (A, F), 5 × $^3/_8$ in. (B, K), 6 × 0.25 in. (I), 6 × $^3/_8$ in. (J), 8 × 0.25 in. (G), 13 × $^3/_8$ in. (H); helium flow rate: 85 ml/hr.

Spectroscopic Analyses.—The infrared spectra of all products were taken as films between sodium chloride disks on a Baird Model 4-55 spectrophotometer. A Varian A-60 nmr spectrometer was used. All nmr spectra were taken in CCl_4 solvent using TMS as internal standard. The ultraviolet spectra of *cis*- and *trans*-β-methylstyrene, respectively, were taken in a 1-cm cell on a Cary 14R recording spectrophotometer in 2,2,4-trimethylpentane solvent purified by passing through silica gel.

Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich., and Micro-Tech Laboratories, Inc., Skokie, Ill. These analyses and refractive indices of the products appear in Table VII.

Registry No.—Styrene, 100-42-5; α-methylstyrene, 98-83-9; *cis*-β-methylstyrene, 766-90-5; *trans*-β-methylstyrene, 873-66-5; **1**, 2057-49-0; **2**, 2057-47-8; **3**, 19991-09-4; **4**, 2057-45-6; **5**, 19991-11-8; **6**, 19991-12-9; **7**, 19991-13-0; **8**, 19991-14-1; **9**, 19991-15-2; **10**, 19991-16-3; **11**, 19991-17-4; **12**, 19991-18-5; **13**, 19991-19-6; **14**, 19991-20-9; **15**, 19991-21-0; **16**, 19991-22-1; **18**, 19991-23-2; **19**, 2110-18-1; **20**, 2110-16-9; **21**, 19991-26-5.