Base-Catalyzed Reactions. XXXIX.[1] Kinetic Studies of Homogeneous Base-Catalyzed Addition Reactions of Alkylaromatics to Conjugated Hydrocarbons

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A large variety of alkylaromatic compounds were found to undergo nucleophilic addition to conjugated olefins at room temperature when the reaction was performed in a dipolar aprotic solvent using potassium *tert*-butoxide as a catalyst. The effectiveness of each of the solvents was determined from pseudo-first-order rate constants for the addition of 4-isopropylpyridine to isoprene in a variety of solvents and it was found to be DMSO > HMPA > NM2P > DMF > TMSO ≈ TMU (NM2P = *N*-methyl-2-pyrrolidone, TMSO = tetramethylene sulfoxide, TMU = tetramethylurea). The rates of reaction were also measured when the conjugated olefin used was styrene, α-methylstyrene, and β-methylstyrene. The mechanism of nucleophilic addition is discussed with regard to the effect of solvent and olefins used. Some selected reactions were run at different temperatures and their activation parameters were calculated.

Pseudohomogeneous alkylation reactions using organoalkali metals as catalysts have been studied extensively in this laboratory and have been shown to be synthetically useful for a variety of reactions.[3] The alkylation reactions were limited mainly to alkylation of alkylbenzenes[3] and alkylpyridines but more recently were also extended to alkylnaphthalenes.[4]

Although high temperatures are necessary for the addition of ethylene to aromatic compounds,[3] it has been found that by substituting conjugated dienes such as butadiene[5] and isoprene[6] or styrenes[7] for ethylene the addition reaction proceeds at room temperature or lower, especially when 2- or 4-alkylpyridines are used as the aromatics. It was thought, therefore, that weaker bases, such as potassium *tert*-butoxide in aprotic solvents, might act as catalysts for the alkenylation or aralkylation of pyridines and of other aromatic compounds. The success of this type of reaction has been reported in a preliminary communication.[8]

The present paper describes the effect of various aprotic solvents on the rate of the homogeneous addition reaction and the activation parameters of some of the reactions in various solutions.

An examination of dipolar aprotic solvents has shown that the negatively charged end of the solvent molecule dipole is more exposed to the molecular environment, and thus the strongest interactions occur with cations.[9] The anions are then free to participate actively in reactions without the stabilizing influence of ion-pair formation; the enhanced reactivity in dipolar aprotic solvents is in many cases quite dramatic. A good review has been written regarding the rates of bimolecular substitution reactions in protic and dipolar aprotic solvents.[10]

Studies have recently been made comparing reactions in various aprotic solvents. Zaugg[11a] investigated the effect of aprotic solvents upon the rate of reaction of sodio-*n*-butylmalonic ester with *n*-butyl bromide and the relative rates follow: benzene, 1; tetrahydrofuran (THF), 14; dimethoxyethane (DME), 80; dimethylformamide (DMF), 970; and dimethyl sulfoxide (DMSO), 1420. The suggested reason for the rate increase is that ionic aggregates are formed in solvents of low dielectric constants, but as the solvent becomes more polar a larger number of very slightly solvated reactive anions are formed that then participate rapidly in the reactions.[11b] In another study of reaction rates in various solvents, it was found that HMPA was a much better solvent than DMSO for the reaction of sodium azide with 1-bromobutane.[12]

Results and Discussion

The variety of alkylaromatics which were alkenylated or aralkylated in a homogeneous solvent–potassium *tert*-butoxide system is given in Table I, and the reactions can be represented by eq 1 and 2.[13]

Several interesting observations can be made from Table I. First, 4-ethyl- and 4-isopropylpyridine (expt 2 and 3) reacted with isoprene rapidly and gave quantitative yields of products in about 15 min. The rate of reaction of 4-picoline was slower than that of the higher 4-alkylpyridines, which is in agreement with the rates of reaction observed previously.[14] It is of interest to note that 2-picoline did not react with isoprene, and the rate of addition of 2-ethylpyridine was substantially slower than that of the 4 isomers in accordance with previous findings.[7]

The use of potassium *tert*-butoxide in a homogeneous system has an advantage in certain cases over the organoalkali metal catalyst systems, insofar as some of the heteroaromatic compounds that failed to react using the organoalkali metal catalysts were found to undergo reaction in a homogeneous medium. One notable example is the reaction of 2-methylthiophene with sty-

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[1] (a) For paper XXXVIII, see W. M. Stalick and H. Pines, *J. Org. Chem.*, **35**, 1712 (1970). (b) Paper X of the series Alkylation of Heteroaromatics; for paper IX, see ref 1a.

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[3] H. Pines and L. A. Schaap, *Advan. Catal.*, **12**, 117 (1960).

[4] B. Stipanović and H. Pines, *J. Org. Chem.*, **34**, 2106 (1969).

[5] H. Pines and J. Oszczapowicz, *ibid.*, **32**, 3183 (1967).

[6] W. M. Stalick and H. Pines, *ibid.*, **35**, 415 (1970).

[7] H. Pines and N. E. Sartoris, *ibid.*, **34**, 2113 (1969).

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

[9] E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 334–342.

[10] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

[11] (a) H. Zaugg, *J. Amer. Chem. Soc.*, **83**, 837 (1961); (b) H. Zaugg, *ibid.*, **82**, 2903 (1960).

[12] J. J. Delpuech, *Tetrahedron Lett.*, 2111 (1965).

[13] While this research was in progress, a condensation of butadiene with compounds of the general structure X–CH_3 (X = NO_2, CN, CHO) was reported: J. E. Hofmann and A. Schriesheim, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 16 (1967).

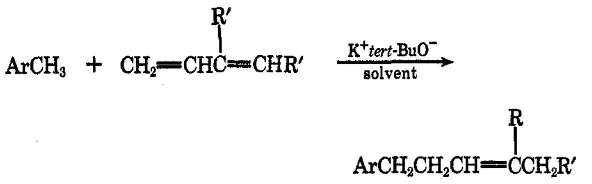
[14] W. M. Stalick and H. Pines, *J. Org. Chem.*, **35**, 422 (1970).

Table I

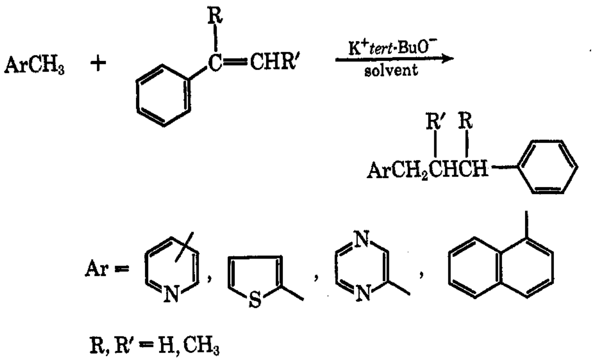
Compounds That Undergo Base-Catalyzed Additions in Homogeneous Systems[a]

Expt no.	Base concn,[b] mol/l.	Alkylaromatic	Alkylaromatic concn, mol/l.	Olefin	Olefin concn, mol/l.	% conversion[c,d]
1	0.5	4-Picoline	3	Isoprene	5	100
2	0.5	4-Ethylpyridine	3	Isoprene	5	100
3	0.5	4-Isopropylpyridine	3	Isoprene	5	100
4	0.5	2-Picoline	3	Isoprene	5	0
5	0.5	2-Ethylpyridine	3	Isoprene	6	15
6	0.5	2-Methylpyrazine	10	Isoprene	10	24
7	0.7	4-Picoline	3	Piperylene	5	77
8	0.7	4-Picoline	3	Butadiene	*e*	51
9	0.5	4-Picoline	10	Styrene	9	76[f]
10	0.5	4-Picoline	10	α-Methylstyrene	8	91[f]
11	0.7	4-Picoline	3	β-Methylstyrene	2.4	65[f]
12	0.7	2-Methylthiophene	3	Styrene	5	10[g]
13	0.7	1-Methylnaphthalene	3	Styrene	5	26[h]
14	0.7	3-Picoline	3	Styrene	5	46[i]

[a] The solvent was HMPA in all cases, and reactions were run at either 20° or room temperature. [b] The catalyst in all cases was potassium *tert*-butoxide. [c] Per cent conversion was based on the amount of alkylaromatic reacted after 3 hr. [d] The products formed were the mono-, di-, and triaddition products produced by adding one, two, or three olefin units to the side chain of the alkylaromatic. [e] Butadiene was bubbled through the reaction mixture as a gas. [f] Per cent conversion in this case is based on the amount of olefin reacted. [g] Yield after 165 hr. [h] Yield after 72 hr. [i] Yield after 50 hr.

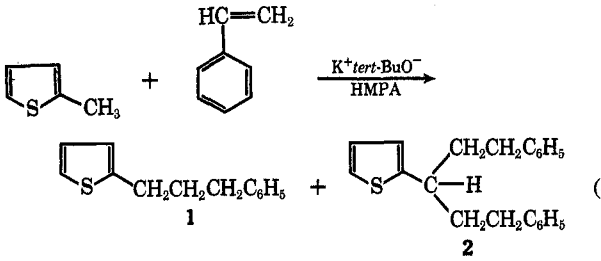


$$\mathrm{ArCH_3} + \mathrm{CH_2{=}CH\overset{R'}{C}{=}CHR'} \xrightarrow[\text{solvent}]{\mathrm{K^+}\textit{tert}\text{-}\mathrm{BuO^-}} \mathrm{ArCH_2CH_2CH{=}\overset{R}{C}CH_2R'} \quad (1)$$



(2)

R, R′ = H, CH$_3$



(3)

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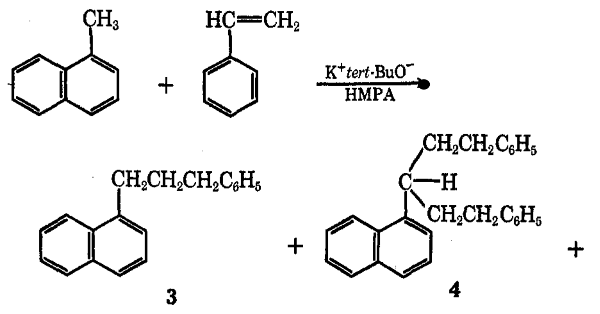
2



3

4

2 minor products (unidentified) (4)

rene (eq 3). Literature reports state that metal hydrogen exchange occurs with the ring hydrogens and not with those of the alkyl side chain.[15] This example seems to be the first report of side chain metalation of one of the five-membered π-excessive heteroaromatic systems. In a like manner, it was possible to alkenylate 2-methylpyrazine (expt 6) and aralkylate 1-methylnaphthalene (eq 4).

The reactions of styrene with 1-methylnaphthalene and 2-methylthiophene were preceded by polymerization of styrene, and only after the styrene slowly depolymerized, after 1 day or longer, was a reaction product formed. Similar observations have been made during aralkylation of alkylpyridines with vinylpyridines.[16]

Finally, all of the conjugated olefins that have been used in the pseudohomogeneous media were found to react in the present system, including isoprene (expt 1), piperylene (expt 7), butadiene (expt 8), α-methylstyrene (expt 10), and β-methylstyrene (expt 11). Some of the yields given in Table I are probably far from optimum, since many of these reactions were run before the best techniques were found.

Kinetic Studies. A. Effect of Solvent on Reaction Rate.—Kinetic studies were made on the reaction of 4-isopropylpyridine with isoprene in a variety of solvents in order to determine their effect on the rate of reaction and product distribution (Table II). As has been reported previously[6] both tail and head addition occur (eq 5). Inspection of Table II shows that the reaction proceeds fastest in DMSO. The solvents were found to support the reaction in the following decreasing order: DMSO > HMPA > NM2P > DMF > TMSO > TMU ≫ ether solvents (NM2P = *N*-methyl-2-pyrrolidone, TMSO = tetramethylene sulfoxide, TMU = tetramethylurea). The present results are in agreement with the data reported for the base-catalyzed isomerization of olefins,[17] but the results are in contradiction with those found by Delpuech[12] who has reported that HMPA was the best

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[15] S. Gronowitz, *Advan. Heterocycl. Chem.*, 73 (1963), and references therein.

[16] N. E. Sartoris and H. Pines, *J. Org. Chem.*, **34**, 2119 (1969).

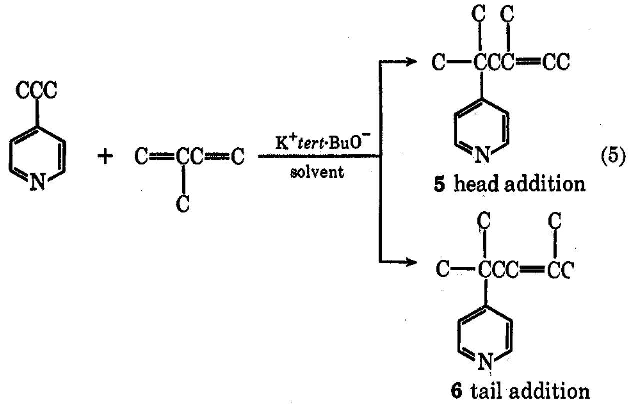
[17] (a) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **87**, 3244 (1965); (b) A. Schriesheim, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, D9 (1969).

TABLE II

EFFECT OF SOLVENT ON REACTION RATE AND PRODUCT RATIO[a] OF 4-ISOPROPYLPYRIDINE WITH ISOPRENE

Expt no.	Solvent[b]	$t_{1/2}$, min	Rate constant[c] × 10^5, sec^{-1}	Products[d] % head addition (5)	Products[d] % tail addition (6)
15	DMSO	1.15	1010	59	41
16	HMPA	1.89	612	41	59
17	NM2P	32.8	35.2	52	48
18	NM2P[e]	36.6	32.0		
19	DMF	70.7	16.4	54	46
20	TMSO	240	4.8	51	49
21	TMU	250	4.66	51	49
22	THF	>1000[f]			
23	*p*-Dioxane	>1000[f]			
24	DME	>1000[f]			

[a] Concentrations used were 4-isopropylpyridine 4.8 mol/l. and isoprene 0.6 mol/l. [l] The catalyst was potassium *tert*-butoxide, concentration 0.45 mol/l. [c] The pseudo-first-order rate contants were determined at 20°. [d] The numbers **5** and **6** refer to the products shown in eq 5. [e] The 4-alkylpyridine used in this case was 4-ethylpyridine. [f] There was no noticeable change in the isoprene concentration after 5 hr.



5 head addition

6 tail addition

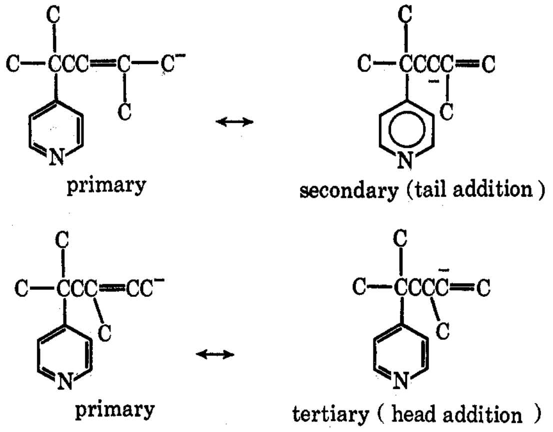
(5)

dipolar aprotic solvent. This was further corroborated by other researchers who observed higher yields for the base-induced alkylation of ethyl acetoacetate in HMPA than in DMSO or NM2P.[18] In the proton exchange reaction of toluene, HMPA is vastly more active than DMSO or TMSO,[19] and again in the base-catalyzed autoxidation of thiols and disulfides HMPA is found to be superior to DMF or TMU.[20] Similar results have led Normant to state that HMPA appears to be the most remarkable of the polar aprotic solvents.[21]

The greater rate enhancement in DMSO over that in HMPA can be explained by considering the free energy *vs.* reaction coordinate of the reaction being studied. The reaction is assumed to proceed from the starting materials through an addition transition state to an intermediate, which will then proceed through a second transition state upon protonation before going to product. It was reported previously from this laboratory[14] that the rate of addition to isoprene was increased in the addition step by metal–double bond complexation and in the protonation step by intramolecular protonation. Any factor that would increase either of these steps would then increase the overall rate of addition.

It is known that, when potassium *tert*-butoxide is employed as a base in DMSO, the latter readily undergoes a proton exchange with alkylaromatics.[22] HMPA, however, does not undergo such an exchange reaction with the surrounding weakly acidic hydrocarbons such as toluene.[19] Considering the addition of the 4-isopropylpyridine anion to isoprene, it is obvious that both DMSO and HMPA are excellent solvents for cation solvation, thus essentially removing the cation from the ion pair. The anion in both of these solvents will therefore readily add to isoprene, but in HMPA the protonation will occur mainly from the excess isopropylpyridine molecules, since *tert*-butyl alcohol generated in the reaction is present only in minute quantities. On the other hand, in DMSO the protonation of the allylic anion can occur not only from isopropylpyridine but also from the solvent itself, thus giving the overall result that DMSO is the best solvent for this reaction.

B. Effect of Solvents on Product Distribution.—The product distribution noted in Table II can also be explained by the ease of protonation of the anion adduct. The addition of the anion to isoprene is assumed to be relatively nonselective in both DMSO and HMPA owing to the absence of ion pairing. Protonation of the anion is, however, sterically more favorable for the head addition isomer. In HMPA, protonation of the anion occurs by the excess 4-isopropylpyridine, and this is a sterically hindered process. In DMSO, however, the intermediate anions can also be protonated by the solvent DMSO, snd these solvent protons are more accessible for protonation. Thus, the product contains more of the tail addition isomer (59%), which, although more sterically hindered for protonation than the head addition isomer, is nevertheless more electronically stable having primary ↔ secondary *vs.* primary ↔ tertiary anions in its resonance state. The other solvents used are intermediate in their abilities to exchange hydrogens, and the product ratios in these solvents are about 50% tail addition and 50% head addition.



C. Effect of Steric Factors on Reaction Rate.—The effects of steric factors on reaction rates were determined using 4-ethyl- and 4-isopropylpyridine as the aromatics and styrene, α-, and β-methylstyrene as the olefins. All rate determinations were made using the 4-alkylpyridine in large excess over the diolefin. Good

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(18) W. J. Le Noble and H. F. Norris, *J. Org. Chem.*, **34**, 1969 (1969).

(19) J. E. Hofmann, A. Schriesheim, and D. D. Rosenfeld, *J. Amer. Chem. Soc.*, **87**, 2523 (1965).

(20) T. J. Wallace and A. Schriesheim, *Tetrahedron*, **21**, 2271 (1965).

(21) H. Normant, *Angew. Chem., Int. Ed. Engl.*, **6**, 1046 (1967).

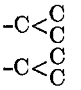
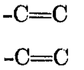
(22) N. Kharasch and B. S. Thyagarajan, *Quart. Rep. Sulfur Chem.*, **1**, 61 (1966).

pseudo-first-order kinetic plots were obtained in all cases.

From Table III it can be seen that the reactions occur fastest in DMSO and HMPA, slower in NM2P, and the slowest in TMU and TMSO. The 4-alkylpyridines added too rapidly to styrene in DMSO or HMPA for the rate of reaction to be measured by the techniques used in this study. The addition of alkylpyridine to pure *cis*- and *trans*-β-methylstyrene could not be studied as these olefins undergo rapid isomerization to a mixture of 95% trans and 5% cis isomer in less than 1 min after contact with the solvent–base system at 20°.

TABLE III

RATES OF REACTION OF ALKYLPYRIDINES WITH STYRENES[a]

Expt no.	x =	x-Alkylpyridine  R =	Styrene  R_1	Solvent	$t_{1/2}$, min	Rate constant[b] × 10^4, sec^{-1}, 10^2
25	4	$\text{-C}<^{C}_{C}$	-C=C	NM2P	0.84	136
26	4	$\text{-C}<^{C}_{C}$	-C=C	TMU	4.60	25.0
27	4	$\text{-C}<^{C}_{C}$	-C=C	TMSO	4.56	25.3
28	4	$\text{-C}<^{C}_{C}$	$\text{-C}\leqslant^{C}_{C}$	NM2P	82.4	1.40
29	4	$\text{-C}<^{C}_{C}$	$\text{-C}\leqslant^{C}_{C}$	DMSO	5.64	20.5
30	4	$\text{-C}<^{C}_{C}$	-C=C-C	DMSO	20.9	5.53
31	4	$\text{-C}<^{C}_{C}$	-C=C-C	HMPA	19.1	6.04
32	4	-C-C	$\text{-C}\leqslant^{C}_{C}$	DMSO	3.36	34.0
33	4	-C-C	-C=C-C	DMSO	3.02	38.3
34	4	-C-C	-C=C	NM2P	1.38	83.7
35	2	-C-C	-C=C	NM2P	40.64	2.82
36	2	-C-C	-C=C	DMSO	4.17	27.4
37	3	-C-C	-C=C	DMSO	17.03	6.78

[a] The catalyst was potassium *tert*-butoxide, concentration 0.45 mol $l.^{-1}$; other concentrations used were 4-isopropylpyridine 4.8 mol $l.^{-1}$, 4-ethylpyridine 5.2 mol l^{-1}, and styrenes 0.6 mol l^{-1}. [b] The pseudo-first-order rate constants were determined at 20.0 ± 0.1°.

Some interesting conclusions can be drawn from the experiments in Table III. 4-Ethylpyridine adds to α-methylstyrene in DMSO 1.7 times as fast as and to β-methylstyrenes 7 times as fast as does 4-isopropylpyridine (expt 29, 30, 32, and 33). This is in contradiction to the results obtained previously from a competitive reaction whereby the 4-isopropylpyridine anion adds to isoprene 1.1 times as fast as does the 4-ethylpyridine anion.[14] The data thus obtained imply that addition to isoprene is the least sterically hindered reaction, whereas the addition to α-methylstyrene must thus be somewhat hindered, and steric hindrance seems to be a major factor in the rate of addition to β-methylstyrene.

The addition of the 4-isopropylpyridine anion to isoprene in DMSO is 1.6 times as fast as that in HMPA, presumably because DMSO aids in the protonation of the product (expt 15 and 16, Table II). When a similar comparison is made for the addition to β-methylstyrene (expt 30 and 31), the reaction rates are about equal with the reaction occurring 1.1 times as fast as that in HMPA, probably because steric hindrance has made the addition step rate controlling.

D. Effect of Acidity on Reaction Rate.—It was found that the rate of addition of the isomeric ethylpyridines to styrene depends on the acidity of the alkylpyridines (Table III). The relative acidities of picolines have been recently determined from the sodium methoxide exchange rates between methanol and ω-tritium-substituted picolines.[23] They were ($K_2 \times 10^6$ l. mol^{-1} sec^{-1}) 3-picoline 0.42, 2-picoline 54, and 4-picoline 760. In the present experiments it was found that the rate of addition of 2-ethylpyridine to styrene is 4 times as great as that of 3-ethylpyridine, although there must be greater hindrance in the addition of 2 over the 3 isomer (Table III, expt 36 and 37).

4-Ethylpyridine adds to styrene in DMSO too fast to be measured, while in NM2P the rate of addition of 4- and 2-ethylpyridine is 83.8 *vs.* 2.84 at 20° (expt 34 and 35). 3-Ethylpyridine is not acidic enough to add to styrene in NM2P; instead the NM2P adds to the olefin to form 3-β-ethyl- and di(3-β-ethyl)-*N*-methyl-2-pyrrolidone.[24]

Activation Parameters.—Table IV summarizes the average rate constants found at the different temperatures and the derived activation parameters as calculated by means of standard expressions. The $\Delta S^{\ddagger}$ values are all negative and show a continuous trend of becoming more negative as the unsaturated hydrocarbons become less sterically hindered to addition in a given solvent, NM2P.

The entropy of activation for the addition of 2- and 4-ethylpyridine to styrene being the same indicates that the lower enthalpy of activation of the 4 isomer is due mainly to its greater acidity and not to a lower steric effect. When a change is made in the solvent for the same reaction, as shown in the first two cases of Table IV, again it is noted that the change in the rate of the reaction is due to the enthalpy of activation. As expected in this study, HMPA has a lower enthalpy of activation and the reaction proceeds faster in this solvent than in NM2P.

Experimental Section

Materials.—Potassium *tert*-butoxide (K & K, dry 99%) was obtained as the sublimed powder and was used without further purification for the synthetic runs but was resublimed before use for the kinetic studies. The solvents DME (Matheson Coleman and Bell), DMF (Baker), DMSO (Matheson Coleman and Bell), *p*-dioxane (Baker), HMPA (Fisher), NM2P (Aldrich), THF (Baker), TMSO (Fairfield Chemical Co.), and TMU (The Ott Chemical Co.) were distilled, dried over Linde 13X molecular sieves, and redistilled immediately before use. The olefins isoprene (Aldrich), piperylene (Matheson Coleman and Bell), butadiene (Matheson), styrene (Eastman), α-methylstyrene (Eastman), and β-methylstyrene (Chemical Samples Co.) were distilled immediately before use. The arylalkanes 4-picoline, 4-ethylpyridine, 2-picoline, 2-ethylpyridine, and 3-picoline (all from Reilly Tar and Chemical Co.), 4-isopropylpyridine (Pfaltz and Bauer), 2-methylpyrazine (Aldrich), 1-methylnaphthalene (Aldrich), and 2-methylthiophene were distilled, dried over Linde 5A molecular sieves, and redistilled immediately before use.

General Reaction Procedure.—The general reaction procedure followed was similar to that used for the isomerization of olefins.[25] All of the needed reagents and solvents were distilled immediately before use and transferred to a drybox where the catalyst solutions were prepared. It has been reported that carbanions in this type of system are relatively stable if oxygen is excluded;[26] these reports were well verified by this study. The alkylaromatic was then added to the catalyst solution contained in a small vial and sealed with a self-sealing neoprene stopper. The sealed vial was

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(23) W. N. White and D. Lazdins, *J. Org. Chem.*, **34**, 2756 (1969).

(24) H. Pines, S. V. Kannan, J. Simonik, and B. Stipanović, unpublished results.

(25) S. Bank, C. A. Rowe, Jr., A. Schrisheim, and L. A. Naslund, *J. Amer. Chem. Soc.*, **89**, 6897 (1967).

(26) A. J. Parker, *Advan. Org. Chem.*, **5**, 1 (1965).

TABLE IV

ACTIVATION PARAMETERS FOR THE ADDITION OF ALKYLPYRIDINES TO ISOPRENE AND STYRENES

Olefin	*x*-Alkylpyridine  *x* =	R =	$K\psi$, sec^{-1}	Temp, °C	Solvent	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg/mol
Isoprene	4	$-C<^{C}_{C}$	3.51×10^{-4} 7.70×10^{-4}	20 30	NM2P	13.8 ± 0.3	13.2 ± 0.3	−29.1 ± 1.1
Isoprene	4	$-C<^{C}_{C}$	3.22×10^{-3} 6.12×10^{-3}	10 20	HMPA	10.6 ± 0.6	10.0 ± 0.6	−34.4 ± 2.3
α-Methylstyrene	4	$-C<^{C}_{C}$	1.40×10^{-4} 3.30×10^{-4}	20 30	NM2P	15.1 ± 0.5	14.5 ± 0.5	−26.6 ± 1.7
Styrene	4	$-C<^{C}_{C}$	8.48×10^{-3} 1.35×10^{-2}	10 20	NM2P	7.8 ± 0.8	7.3 ± 0.8	−42.3 ± 2.7
Styrene	2	-C-C	2.82×10^{-3} 6.06×10^{-4}	20 30	NM2P	13.4 ± 0.2	12.83 ± 0.23	−31.0 ± 0.8
Styrene	4	-C-C	5.03×10^{-3} 8.38×10^{-2}	10 20	NM2P	8.7 ± 0.02	8.20 ± 0.02	−31.8 ± 0.1
Styrene	3	-C-C	2.24×10^{-4} 6.78×10^{-4}	10 20	DMSO	9.6 ± 0.2	9.06 ± 0.21	−33.9 ± 0.8

then removed either to the laboratory or placed in a thermostated constant temperature bath. The olefin was injected through the neoprene cap and reaction samples were removed at various intervals and quenched in methanol. The samples were then analyzed for products by vpc. When preparative samples were prepared, the reactions were quenched with methanol and extracted with water and ether. The ether fractions were combined and dried over $MgSO_4$, and the ether was removed by rotary evaporation before the residue was distilled for a crude separation of products. Further purifications were made by preparative vpc.

Characterization of Compounds in Table I.—1-Phenyl-3-(2-thienyl)propane (**1**) and 1,5-diphenyl-3-(2-thienyl)pentane (**2**) were synthesized by the general reaction procedure given above. After the solvent had been removed, compound **1** distilled over as a light yellow fraction at 124° (5 mm). Compound **2** was left in the brown residue after distillation. Further purification of compound **1** was made by vpc using an 8 ft × $^3/_8$ in. column packed with 15% silicone gum rubber SE-30 on 60–80 mesh Gas-Pack WAB at 220°. The nmr spectrum was taken and found to be consistent with the proposed structure. Compound **2** was purified on the same preparative pvc column at 250°, and after two recyclings a clear, viscous liquid was obtained in 99.5+% purity. The spectrum was taken using a micro nmr tube and found to be consistent with the proposed structure.

In a like manner 1-phenyl-3-(1-naphthyl)propane (**3**) and 1,5-diphenyl-3-(1-naphthyl)pentane (**4**) were synthesized and identified. Purification was made on the vpc column described above. Compound **3** was purified at 240° and compound **4** at 270°. Two other higher boiling minor products were evident but were not separated for identification. The nmr spectra of both **3** and **4** were consistent with the proposed structures.[27]

The other reactions described in Table I were not run on a preparative scale since the products of reaction have previously been reported. Product identifications were for the most part made by comparative vpc with compounds of known structure. The products from the following reactants are reported: 4-picoline with piperylene,[28] butadiene,[5,14] styrene,[7] α-methylstyrene,[7] and β-methylstyrene;[7] 4-picoline, 4-ethylpyridine, and 4-isopropylpyridine with isoprene;[6] and 3-picoline with styrene.[29]

Calculations.—After the samples taken from the reactions studied at different time intervals were analyzed, the data were transferred to computer cards. The reaction rate constant and half-life were then calculated by means of the FORTRAN program TXNRAT, using standard least-squares techniques.[30] Activation parameters were then calculated by means of standard expressions. All calculations were carried out on the Northwestern University CDC 6400 computer.

Equipment.—Nmr analyses were performed on a Varian Model A-60 spectrophotometer using tetramethysilane as an internal standard in a CCl_4 solvent. The micro nmr tube was from NMR Specialties, Inc. Some studies were performed at a constant temperature in a Lo-Temptrol 154 constant temperature bath from Precision Scientific Co. thermostated to ±0.10°. Vpc separations and identifications were made using an F & M Model 270 dual-column gas chromatograph equipped with a thermal conductivity detector and using helium as a carrier gas. Product compositions, separations, and identifications were performed using 7 ft × 0.25 in. or 8 ft × $^3/_8$ in. columns packed with 15% silicone gum rubber SE-30 on 60–80 mesh Gas-Pack WAB and a 10.5 ft × 0.25 in. column packed with 15% Versamid 900 on 60–80 mesh Gas-Pack WAB at various temperatures.

Registry No.—**1**, 29908-27-8; **2**, 29908-28-9; **3**, 29908-29-0; **4**, 29908-30-3; 4-picoline, 108-89-4; piperylene, 504-60-9; butadiene, 106-99-0; styrene, 100-42-5; α-methylstyrene, 98-83-9; β-methylstyrene, 637-50-3; 4-ethylpyridine, 536-75-4; 4-isopropylpyridine, 696-30-0; isoprene, 78-79-5; 3-picoline, 108-99-6; 2-picoline, 109-06-8; 2-ethylpyridine, 100-71-0; 3-ethylpyridine, 536-78-7.

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[27] By vpc compounds **1–4** were found to be of greater than 95% purity. Using nmr it was then possible to determine accurately the number of styrene moieties that had been added to the alkyl side chain.

[28] H. Pines and B. Stipanović, unpublished results.

[29] Yu. I. Chumakov and V. M. Ledovskikh, *Tetrahedron*, **21**, 937 (1965).

[30] A modification of a program reported earlier: J. P. Day, F. F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 6927 (1968).