formed under kinetic control, and this adjusts in favor of the 1,4 isomer to give a different mixture under thermodynamic control. In no case was the exclusive formation of one isomer observed either initially or in the equilibrium mixture. There is an indication that the 1,2 isomer is less favored for the *N*-benzyl derivatives compared to the corresponding *N*-methyl derivatives both initially and in the equilibrium mixtures, which may be due to steric interactions. However, it should be noted that only very small differences in energy would be needed to cause these changes.

In all cases, the 1,2 isomer absorbs at higher wavelength than the 1,4 isomer and both isomers show single absorptions. It is thought that one of the most important applications of the flow NMR technique has been the unambiguous assignment of UV–vis absorptions which now makes possible kinetic studies in dilute, ideal solutions.

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Registry No.—Methoxide, 2143-68-2.

References and Notes

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Nuclear Magnetic Resonance Investigation of the Adducts Formed by the Attack of Carbanions on Substituted Pyridinium Ions[1,2]

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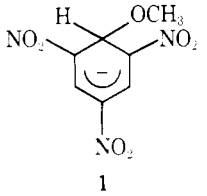
High-resolution NMR has been used to characterize the adducts formed by the attack of nitroalkane carbanions on 3-substituted and 3,5-disubstituted pyridinium ions in aqueous solution and to assign their UV–vis spectra. In all cases studied, only the 1,4-dihydro compound formed by attack of the nucleophile at the 4 position in the ring was found, suggestive of either a very fast isomerization and extreme thermodynamic stability of the 1,4-dihydro compound or a specific interaction between the pyridinium cation and the attacking nucleophile which yields only a single isomer under kinetic control.

In the previous paper we have presented the results of a flow NMR investigation of the attack of alkoxide ions on substituted pyridinium ions carried out to try to determine the relationship between the kinetic and thermodynamic distributions of the isomers formed. It was found that a mixture of 1,2 and 1,4 isomers was formed under kinetic control and that this adjusted in favor of the 1,4 isomer to give the final thermodynamically stable mixture of isomers. In the present paper we present the results of another approach to this problem using the carbanions formed from nitroalkanes as the attacking nucleophiles where it was hoped, on the basis of previous work on nitroaromatic compounds, that there would be no further reaction of the mixture formed under kinetic control.

There exist several examples of the relative stability of the adducts of carbanions with nitroaromatics: Thus, the methoxide adduct **1** of 1,3,5-trinitrobenzene will react with acetone to produce the corresponding acetonate ion adduct **2**, but this reaction cannot be reversed, nor is there any exchange with CD_3COCD_3 even in the presence of base.[4] Similar reactions are observed with the adducts formed by attack of carbanions formed from nitroalkanes.[5]



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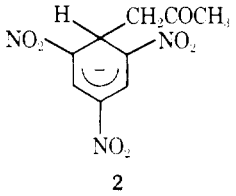

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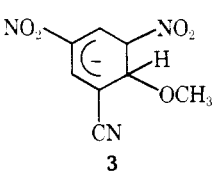
Further, if an unsymmetrical nitroaromatic is used, e.g., 3,5-dinitrocyanobenzene, attack of alkoxide ion yields the thermodynamically stable mixture of isomers, in this case almost exclusively the isomer **3**.[6] It has more recently been shown by stopped-flow UV–vis spectroscopy and flow NMR spectroscopy that under kinetic control a mixture of the two isomers **3** and **4** is in fact formed which then extremely rapidly



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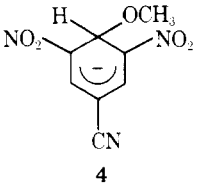

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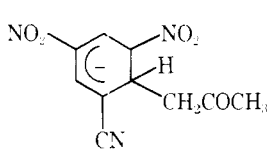
isomerizes to give the thermodynamically stable mixture consisting almost entirely of **3**.[7]

However, when acetonate ion is used as nucleophile, a mixture of **5** and **6** is formed of almost the same proportions as the kinetic mixture of **3** and **4** and no isomerization is observed.[6] Similar results are observed for nitroalkane anions.[5] Further, the same mixture of **5** and **6** is obtained by reaction



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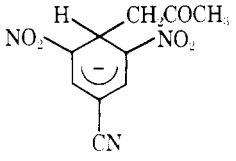

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of **3** with acetone or nitroalkanes, suggesting that this type of reaction occurs by disproportionation of the alkoxide complex back to reactants and then carbanion attack rather than by any type of displacement reaction.

Thus, in a general sense, it was felt that carbanion nucleophiles were acting as "probes" for distribution of products formed under kinetic control in the attack on nitroaromatics and that they might yield information about the initial distributions of isomers in the reactions of pyridinium ions. Nitroalkane anions were chosen as the carbanion species as they could be easily isolated as pure compounds and were soluble in aqueous solution.

Experimental Section

High-resolution NMR spectra were obtained using a Varian H.A. 100 spectrometer, UV–vis spectra on a Unicam SP800 spectrophotometer, IR spectra on a Beckman I.R.5 spectrophotometer and mass spectra on a Varian CH7 mass spectrometer. Pulse-FT ^1H NMR spectra were obtained using a Bruker WP60 spectrometer.

Pyridinium ions were prepared by conventional techniques from commercially available starting materials and had NMR and other spectral properties characteristic of their proposed structures. 18-Crown-6 ether was purchased from P.C.R. Incorporated, Fla. *N*-Methyl-3,5-dinitropyridinium *p*-toluenesulfonate was prepared by fusing 3,5-dinitropyridine overnight at 104 °C with methyl *p*-toluenesulfonate. The resultant salt (95% yield) melted at 235–240 °C. The NMR spectrum (Me_2SO-d_6) showed signals at δ 10.24 (doublet) and δ 9.50 (triplet) due to the hydrogens of the *N*-methyl-3,5-dinitropyridinium ion and signals at δ 7.10, 4.56, and 2.30 due to the ring hydrogens of the *p*-toluenesulfonate ion and the two methyl groups.

The nitroalkane salts were prepared by the following general technique: An ice-cold solution of sodium methoxide in absolute methanol was added in one portion to a molar equivalent of the nitroalkane in ice-cold methanol. A small quantity of white solid precipitated and after the solution had stood for 30 min, dry ether was added to precipitate the remainder of the product. The resulting white solid was filtered, washed well with anhydrous ether, and dried in a desiccator under high vacuum. Yields were usually about 60%. Deuterated nitroethane anion $CH_3CD^-NO_2$ was prepared by warming a solution of $CH_3CH^-NO_2$ in D_2O on a water bath for 15 min. The extent of deuteration was checked by ^1H NMR.

The adducts were prepared by the following general procedure: Aqueous solutions of the pyridinium salt and the salt of the nitroalkane anion were mixed at room temperature. There was immediate precipitation of the adduct. In the case of 1-methyl-3,5-dinitropyridinium *p*-toluenesulfonate and 1-methyl-3,5-dicyanopyridinium *p*-toluenesulfonate, yellow solids were produced and these were filtered and dried. In other cases, the adducts were formed as oils which were extracted with chloroform. The chloroform solution was dried and the chloroform evaporated. The adducts were identified by their IR, NMR, and mass spectra and by chemical analysis (C,H,N); yields were quantitative. 18-Crown-6 ether was purchased from P.C.R. Incorporated, Fla.

Results and Discussion

As discussed in the preceding paper, in the case of the reaction of 3-substituted pyridinium ions, the position of attack cannot be unambiguously deduced from consideration of the ^1H NMR spectra alone, and recourse must be made to isotopic substitution. Such substitution experiments were carried out on all the compounds studied.

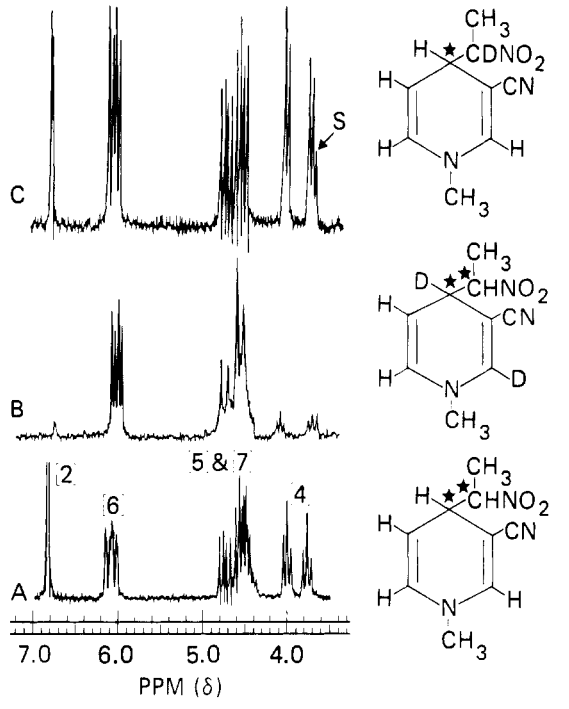


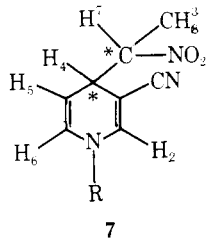
Figure 1. 100 MHz NMR spectra of the adduct formed by action of nitroethane anion on 3-cyanopyridinium methiodide. Spectra recorded in $CDCl_3$: (A) undeuterated reactants; (B) 2,4-dideuterated-3-cyanopyridinium methiodide plus nitroethane anion; (C) 3-cyanopyridinium methiodide plus deuterated nitroethane anion.

A. 3-Cyanopyridinium Ions Plus Nitroalkane Anions. The bottom spectrum in Figure 1 is that of the adduct formed by the reaction of 3-cyanopyridinium methiodide with nitroethane anion. The three possible adducts which could have been formed are **7**–**9**.

As can be seen from the figure, there has been a large upfield shift of all the signals from those of the parent pyridinium ion consistent with there being attack on the ring, disruption of the ring current, and removal of the positive charge. Compound **9** is ruled out for this species as H_2 appears at low fields. One apparent anomaly in the spectrum is the "doubling" of all the peaks. This cannot be due to a mixture of **7** and **8** as within each pair of multiplets the couplings would be different.

The second spectrum in the series is that of the adduct from the corresponding 2,4-dideuteriopyridinium ion. This allows the assignment of H_4 in the bottom spectrum. The top spectrum is that of the adduct from the attack of $CH_3CD^-NO_2$ and allows the assignment of the signal due to the hydrogen H_7 in the nitroalkane moiety; it also clearly indicates that this hydrogen is strongly coupled into H_4 on the ring. This means that the adduct must be compound **7**, R = CH_3.

The apparent doublet splittings in the spectrum are due to the existence of diastereomers of the adduct. Thus, C_4 in the ring and the tertiary carbon in the nitroalkane moiety are both



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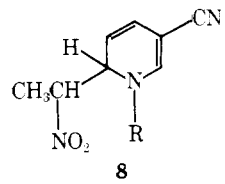

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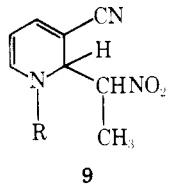

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Table I. Proton Chemical Shifts (ppm) from Tetramethylsilane of the Nitroalkane Adducts of 3-Cyanopyridinium Cations

adduct[a,b]	registry no.	H_2	H_4	H_5	H_6	H_7	H_8
7 a_1	68843-34-5	6.8_2	3.9_9	4.5_1	6.1_0	4.4_1	1.5_3
a_2	68843-35-6	6.8_2	3.7_5	4.6_9	6.0_6	4.5_4	1.5_3
b_1	68843-36-7	6.8_5	4.0_2	4.5_5	6.1_4	4.4_5	1.5_2
b_2	68843-37-8	6.8_5	3.7_8	4.7_3	6.1_0	4.5_9	1.5_2
c_1	68843-38-9	6.7_6	3.9_3	4.4_4	6.0_0	4.3_1	1.4_3
c_2	68854-49-9	6.7_6	3.6_8	4.6_3	5.9_5	4.4_3	1.4_3
d_1	68843-39-0			4.5_1	6.1_0	4.4_1	1.5_3
d_2	68854-48-8			4.6_9	6.0_6	4.5_4	1.5_3
10[c]		6.70	4.00	4.73	5.96	4.41	

[a] Coupling constants for 7: a_1, $J_{H_2-H_6} = 1.4$, $J_{H_5-H_6} = 7.7$, $J_{H_4-H_6} = 0.6$, $J_{H_4-H_5} = 4.3$; a_2, $J_{H_2-H_6} = 1.4$, $J_{H_5-H_6} = 7.7$, $J_{H_4-H_6} = 0.6$, $J_{H_4-H_5} = 4.6$. [b] a: R = CH_3. b: R = CH_2CH_3. c: R = $CH_2CH_2CH_3$. d: R = $CH_2C_6H_5$. [c] Registry No.—10 (a, R = CH_3), 68843-40-3. 10 (b, R = CH_2CH_3), 68843-41-4. 10 (c, R = $CH_2CH_2CH_3$), 68843-42-5. 10 (d, R = $CH_2C_6H_5$), 68843-43-6.

Table II. Proton Chemical Shifts (ppm) from Tetramethylsilane of the Nitroalkane Adducts of 3,5-Disubstituted Pyridinium Cations

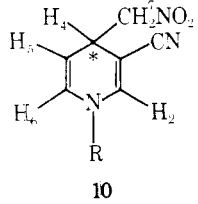
adduct	X, R	registry no.	solvent	H_2H_6	H_4	H_7	H_8
11[a]	Cl, $-CH_3$	68843-44-7	$CDCl_3$	6.2_5	4.4_8	4.6_9	1.5_5
11	Cl, $-CH_2CH_2CH_3$	68843-45-8	$CDCl_3$	6.2_6	4.4_9	4.7_1	1.5_8
11	Cl, $-CH_2C_6H_5$	68843-46-9	$CDCl_3$	6.2_5	4.4_8	4.7_0	1.5_6
11	CN, $-CH_3$	68843-47-0	$CDCl_3$	6.7_5	*b*	*b*	1.7_2
11	CN, $-CH_3$		Me_2SO-d_6	7.5_3	4.3_5	4.6_2	1.5_2
11	NO_2, CH_3	68843-48-1	Me_2SO-d_6	7.2_4	5.3_2	4.6_4	1.3_2
12	Cl, CH_3	68843-49-2	$CDCl_3$	6.2_3	4.1_8		4.7_4

[a] Coupling constants (Hz) for 11 (X = Cl; R = $-CH_3$) $J_{H_7-H_8} = 3.4$, $J_{H_4-H_7} = 1.2$, $J_{H_2-H_6} = 1.4$. [b] Could not be resolved due to low intensity.

asymmetric carbons and diastereomers are produced. These assignments were confirmed by spin-decoupling experiments. They are further confirmed by experiments using nitromethane anion where no asymmetric carbon is produced on the nitroalkane moiety of the adduct (see on).

Very similar spectra were obtained for the adduct formed by attack of nitroethane anion on *N*-benzyl-3-cyanopyridinium chloride. The spectral data are summarized in Table I. There is again a "doubling" of the spectrum due to the existence of diastereomers, and the data are completely consistent with the adduct being again the 1,4-dihydro adduct 7, R = benzyl.

Attack of nitromethane anion on 3-cyanopyridinium methiodide gives an adduct which shows a very similar spectrum to those described above. The spectral parameters are listed in Table I, and deuteration experiments indicate that again the attack has taken place at C_4 to yield the 1,4-dihydro adduct **10**, R = CH_3. As expected, there is no "doubling" of



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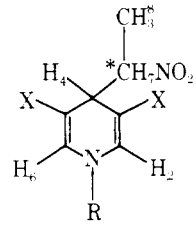
this spectrum as diastereomers are no longer possible, the nitroalkane moiety no longer containing an asymmetric carbon.

B. Reaction of 3,5-Disubstituted Pyridinium Ions with Nitroalkane Anions. In the case of symmetrically substituted pyridinium ions, there is no ambiguity in the deduction of the point of attack from the NMR spectral data, but deuteration experiments have been carried out to simplify the detailed interpretation of the spectra.

Spectrum A in Figure 2 is that of the adduct from the attack of nitroethane anion in 3,5-dichloropyridinium methiodide and shows absorptions at δ 6.25 and 4.48 for the ring protons. There is a marked upfield shift of the ring proton signals from that of the parent pyridinium ion again consistent with the disruption of the ring current and removal of the positive charge from the system. The spectrum indicates that the attack has taken place at C_4 to yield 11 (R = CH_3; X = Cl).



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The assignment is confirmed by the use of the 2,6-dideuterated pyridinium ion (Figure 2B) and by use of $CH_3CD^-NO_2$ (Figure 2C) and the spectral parameters are presented in Table II. That the inequivalence of the ring protons H_2 and H_6 giving rise to the AB multiplet in the spectrum is due to the presence of the asymmetric carbon in the nitroalkane moiety and not attack at any other position is confirmed by the deuteration experiments. It is further substantiated by the use of nitromethane anion (see on). Very similar spectra are given by the adduct from the attack of nitroethane anion on *N*-benzyl-3,5-dichloropyridinium chloride, consistent with there having been attack at C_4 to yield 11 (R = benzyl; X = Cl). The spectral parameters for this adduct and also that from the attack of nitromethane anion on 3,5-

Table III. UV-Vis Spectral Data for the Adducts Formed by the Action of Nitroethane Anion on 3-Cyano- and 3,5-Dichloropyridinium Ions at 30 °C in the Solvents Indicated

compd	solvent	λ_1, nm	λ_2, nm	ϵ_{max_1}	ϵ_{max_2}
7, R = $-CH_3$	Me_2SO	326		5460	
7, R = $-CH_3$	$CHCl_3$	324		5740	
7, R = $-CH_2C_6H_5$	Me_2SO	325		6200	
11, X = -Cl; R = $-CH_3$	Me_2SO	303	355	3916	1283
11, X = -Cl; R = $-CH_3$	$CHCl_3$	303	354	3850	1150
11, X = -Cl; R = $-CH_2C_6H_5$	Me_2SO	304	353	3870	1310

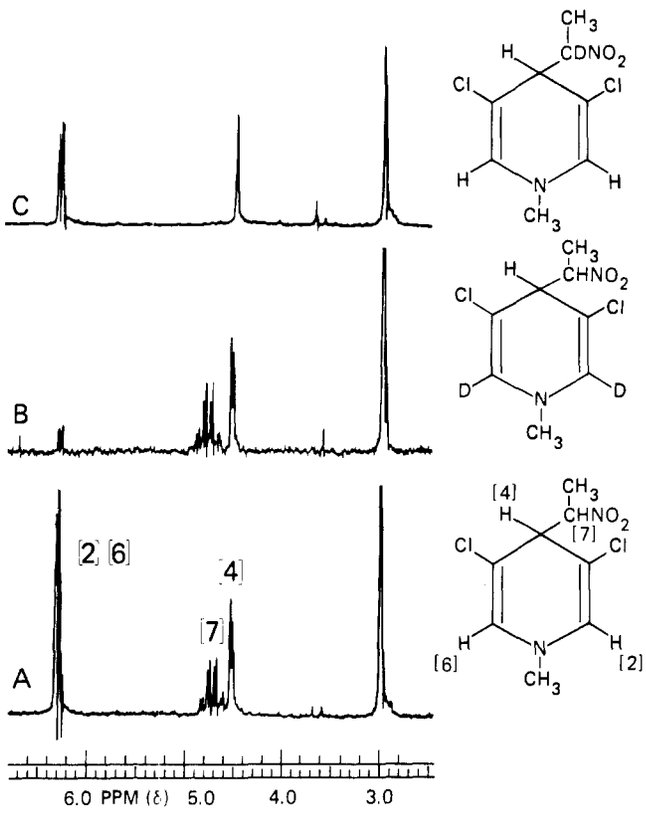
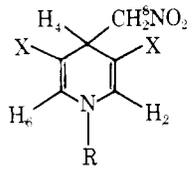


Figure 2. 100 MHz NMR spectra of the adduct formed by action of nitroethane anion on 3,5-dichloropyridinium methiodide. Spectra recorded in $CDCl_3$: (A) undeuterated reactants; (B) 2,6-dideuterated-3,5-dichloropyridinium methiodide plus nitroethane anion; (C) 3,5-dichloropyridinium methiodide plus deuterated nitroethane anion.

dichloropyridinium methiodide are listed in Table II. In the latter case, the spectrum is again in agreement with an attack at C_4 to yield **12** (R = CH_3; X = Cl). In this spectrum H_2 and H_6 are now equivalent as the nitroalkane moiety no longer contains an asymmetric carbon atom.



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The reactions of nitroethane anion with 1-methyl-3,5-dicyanopyridinium *p*-toluenesulfonate and 1-methyl-3,5-dinitropyridinium *p*-toluenesulfonate were also investigated to see if the presence of two very strongly electron withdrawing groups in the 3 and 5 positions might lead to attack at positions 2 and 6. In these cases, the adducts were crystalline solids. The NMR spectral data are summarized in Table II and again are diagnostic of attack only at carbon 4 yielding **11** (R = CH_3; X = CN and R = CH_3; X = NO_2, respectively).

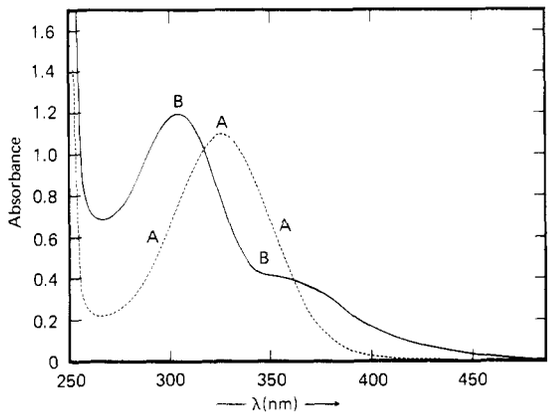


Figure 3. UV-vis spectra in Me_2SO solution of adducts formed by action of nitroethane anion on substituted pyridinium ions: (A) structure 7, R = CH_3; (B) structure 11, X = Cl; R = CH_3.

C. Experiments Using 18-Crown-6 Ether. Experiments were carried out using 1:1 complexes of 18-crown-6 ether with the potassium salts of nitromethane and nitroethane anions. The use of these complexes made it possible to investigate the reactions in a series of nonaqueous solvents, namely benzene, acetonitrile, and dimethyl sulfoxide. Under these conditions the products and reactants were all soluble in the reaction mixture and the complexes formed were not isolated but identified "in situ" using the previous spectral data.

In all cases, only the 1,4-dihydro-substituted pyridine was formed, suggesting that it was unlikely that the isolation of the single isomer in the case of the reaction in aqueous solution was an artifact due to a very limited solubility of the 1,4-dihydropyridine isomer compared to the 1,2-dihydropyridine isomer.

D. UV-Vis Spectral Assignments. The UV-vis spectra of the adducts were measured first as a check of general observations in the literature concerning dihydropyridine systems and second to characterize them to facilitate further investigation of these systems by UV-vis spectroscopy and stopped flow techniques at much lower concentrations where the adducts might well be soluble.

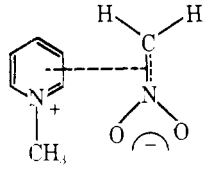
The UV-vis spectra of two typical systems are shown in Figure 3 and a complete listing of the spectral parameters given in Table III.

The adducts from attack on 3-cyanopyridinium ions show a single absorption maximum at about 325 nm whereas those from 3,5-dichloropyridinium ions give rise to two absorptions at about 300 and 350 nm. Absorption at 250–300 nm is frequently present in cross-conjugated 1,2- or 1,6-dihydropyridines and this is often used to distinguish 1,2 and 1,6 isomers from 1,4 isomers which are reported to display a two-banded spectrum.[8] These generalizations are clearly not borne out in the present work where the isomers have all been clearly identified by NMR as 1,4 isomers and the data indicate the problems inherent in the assignment of structure to compounds of this type purely on the basis of their UV-vis spectra. The data in Table III were obtained using very dilute solutions

($\sim 10^{-4}$ M) whereas the NMR data were initially obtained on much more concentrated solutions. A direct comparison was made by recording the NMR spectra on the same solutions used for the UV–vis spectroscopy using pulse-Fourier transform techniques to give sufficient S/N enhancement in the ^{1}H NMR spectra. The NMR spectra were identical to those obtained previously, taking into account the change in operating frequency between the two spectrometers, indicating that only the 1,4 isomer was present.

E. Conclusions. The NMR spectra of the adducts clearly indicate that in every case the only compound isolated was the adduct from attack at C_4 in the pyridinium-ion ring. It is possible that a very fast isomerization reaction takes place, although this seems unlikely as no other isomers were found in any of the systems in what would be the equilibrium mixture and also because of the observations made on analogous reactions of nitroaromatics with carbanions referred to in the introduction.

Another possibility is that there is only one isomer formed in the reaction, suggesting a very specific interaction between the two components prior to the attack of the nucleophile on the ring. This is reminiscent of the suggestion of Kosower[9] that specific charge-transfer interaction might influence these reactions. It should be noted that although the example chosen by Kosower[10] is probably a δ complex,[11] this does not invalidate the idea itself of a specific orientation of the two components in the reaction determining the position of attack. The appropriate complex for these components could be **13**,



13

where the σ carbon of the nitroalkane anion would be well oriented for the attack to occur at C_4. Independent of the reason, the results do suggest that there can be specific orientation of attack in some cases, contrary to the ideas of Lyle.[12]

For the two nucleophiles studied, two different types of behavior have been found and further investigation of these related systems by stopped flow techniques using UV–vis spectroscopy using the spectral assignments given would be warranted as would also studies of the reactions of other nucleophiles with these substrates where the position(s) of attack is clearly defined by deuterium labeling and NMR spectroscopy. A decision involving the different factors governing the position of nucleophilic attack on these substrates[9,12,13] will more easily be made when the experimental data are unambiguous.

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Registry No.—*N*-Methyl-3,5-dinitropyridinium *p*-toluenesulfonate, 68843-50-5; 3,5-dinitropyridine, 940-06-7; methyl *p*-toluenesulfonate, 80-48-8; nitromethane, 75-52-5; nitroethane, 79-24-3; deuterated nitroethane anion, 68843-51-6; 3-cyanopyridinium methiodide, 1004-16-6; 1-ethyl-3-cyanopyridinium, 68843-52-7; 1-propyl-3-cyanopyridinium, 68843-53-8; *N*-benzyl-3-cyanopyridinium chloride, 14535-08-1; nitroethane anion, 25590-58-3; nitromethane anion, 18137-96-7; 3,5-dichloropyridinium methiodide, 23029-86-9; 1-propyl-3,5-dichloropyridinium, 68843-54-9; *N*-benzyl-3,5-dichloropyridinium chloride, 68843-55-0; 3,5-dicyanopyridinium methyl *p*-toluene sulfonate, 15834-67-0; 18-crown-6 ether 1:1 complex with the potassium salt of nitromethane anion, 68844-28-0; 18-crown-6 ether 1:1 complex with the potassium salt of nitroethane anion, 68844-29-1.

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Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Effects of Hydrogen Bonding and Protonation on Nitrogen Chemical Shifts of Pyrazoles[1]

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The ^{15}N chemical shifts of pyrazole, *N*-methylpyrazole, 3-methyl- and 3,5-dimethylpyrazoles, and indazole have been measured as a function of solvent and acidity of the medium. Hydrogen bonding and protonation result in upfield shifts of both the pyridine- and pyrrole-type nitrogen resonances of these substances with the effect being larger at the pyridine-type nitrogens. The protonation shifts far exceed those resulting from hydrogen bonding.

The value of ^{15}N NMR spectroscopy in elucidating effects of hydrogen bonding and protonation in diazoles has been clearly demonstrated for imidazoles.[2,3] Because of the proximity of their nitrogens, pyrazoles should be especially interesting in this respect as suggested by the data on the effects of solvents on the ^{14}N shifts[4] of pyrazole, indazole, and their *N*-methyl derivatives.

Several pyrazoles have been studied by ^{13}C NMR.[5,6] How-

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