J. Am. Chem. Soc. 1983, 105, 90-96

# Kinetics and Mechanism of the C-Alkylation of Nitroalkane Anions by 1-Alkyl-2,4,6-triphenylpyridiniums: A Nonchain Reaction with Radicaloid Characteristics[1]

**Alan R. Katritzky,* M. Akram Kashmiri, George Z. de Ville, and Ranjan C. Patel**

*Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611, and the School of Chemical Sciences, University of East Anglia, Norwich, England.*

*Received September 14, 1981*

**Abstract:** The C-alkylation of 2-nitropropanide by N-substituted pyridiniums is first order in each reactant in $Me_2SO$. The effect on the rate of temperature, N substituent, leaving group, and nucleophile was studied quantitatively. Overall, the evidence excludes an $S_N2$ displacement and suggests that the reactions proceed by a free radical nonchain mechanism.[†]

We have shown[2] that the reaction of *N*-(primary alkyl)-, *N*-(secondary alkyl)-, and *N*-benzyl-2,4,6-triphenylpyridiniums (**1**) with nitronate anions **2a–c** derived from nitromethane, nitroethane, and 2-nitropropane yields the corresponding C-alkylated nitro compounds **6** in preparatively useful reactions (Scheme I). We now report kinetic studies with sodium 2-nitropropanide (**2c**) and nitromethanide (**2a**) as nucleophiles in $Me_2SO$ solution designed to clarify the mechanisms of these reactions.

**Preparative Work.** The pyridiniums used were prepared by standard methods.[3] Some preparative reactions between the pyridiniums (**1**) and nitroalkane anions (**2**) have not previously been reported. *N*-(*p*-Nitrobenzyl)-2,4,6-triphenylpyridinium (**1e**) with **2c** gives 2-(*p*-nitrobenzyl)-2-nitropropane (80%), with melting point in agreement with the literature.[4] Similarly, the *N*-methylpyridinium **1f** gave 2-methyl-2-nitropropane (57%). *N*-(Neopentyl)-2,4,6-triphenylpyridinium (**1j**) with 2-nitropropanide (**2c**) gave 2,4,4-trimethyl-2-nitropentane in 50% yield.

Reaction of *N*-(4-methoxybenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate with **2c** at 25 °C gave 4-anisaldehyde (69%), the significance of which is mentioned later. Sodium nitromethanide reacts at 25 °C under $N_2$ in $Me_2SO$ with the *N*-benzyl compound **1a** to give 2-phenylnitroethane in 58% yield. In air, only a very low yield (ca. 6%) of 2-phenylnitroethane was isolated: a separate experiment showed that in alkaline $Me_2SO$, where air was passed, 2-phenylnitroethane had a half-life of a few hours only. Sodium nitromethanide decomposes quickly in the presence of air in an alkaline medium.

**Kinetic Studies of the Reaction of 1-Benzyl-2,4,6-triphenylpyridinium with Sodium 2-Nitropropanide.** The kinetic runs reported were carried out in $Me_2SO$ containing 2% *n*-pentanol under pseudo-first-order conditions (excess of 2-nitropropanide) and followed by UV. Good reproducibility was obtained with the pyridinium and 2-nitropropane under these conditions and also with pentanol as solvent. The results of a typical experiment are given in the supplementary material (Table A); the pseudo-first-order dependence is illustrated in Figure 1. Figure 2 demonstrates that at various temperatures the rate is proportional to the nucleophile concentration. Observed rates and derived second-order rate constants are collected in Table I.

The Arrhenius plot is shown in Figure 3. A good straight line is obtained from 25-50 °C, but at 70 °C the rate goes very fast indeed (for discussion, see later). From Figure 3 we calculate $E_a = 4.3 \pm 0.6$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -58 \pm 2$ cal mol$^{-1}$ K$^{-1}$.

Reaction of 1-benzyl-2,4,6-triphenylpyridinium with sodium 1-nitrocyclohexanide gave very similar kinetic results (Table II) with $k_2$ a little larger.

Scheme I

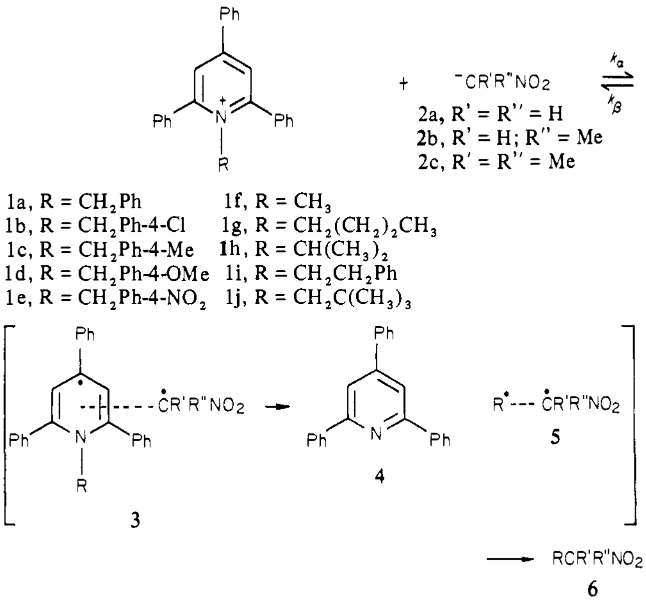


Table I. Temperature Dependence of Second-Order Rate Constants[a] for the Reaction of 1-Benzyl-2,4,6-triphenylpyridinium Tetrafluoroborate[b] with Sodium 2-Nitropropanide in $Me_2SO$ (Measured at 312 nm)

| temp, °C | [Nu$^-$], $10^3$ M | no. of runs | $k_{obsd}$, $10^3$ s$^{-1}$ (*r*) | $k_2$, L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 25[c] ± 1 | 0.50 | 1 | 1.86 (0.992) | 3.72 |
| | 0.83 | 1 | 2.99 (0.995) | 3.60 |
| | 0.99 | 1 | 3.52 (0.998) | 3.55 |
| | 1.06 | 4 | 3.44[e] (0.999)[e] | 3.25[e] |
| | 1.15 | 1 | 4.09 (0.998) | 3.55 |
| | 1.32 | 1 | 5.29 (0.995) | 4.01 |
| | 1.48 | 1 | 5.52 (0.998) | 3.72 |
| | 1.65 | 1 | 6.19 (0.995) | 3.75 |
| 30 ± 1 | 1.06 | 3 | 3.72[e] (0.999)[e] | 3.53[e] |
| 40 ± 1 | 1.06 | 3 | 4.86[e] (0.999)[e] | 4.60[e] |
| 50[d] ± 1 | 0.33 | 1 | 1.92 (0.992) | 5.81 |
| | 0.50 | 1 | 2.89 (0.993) | 5.78 |
| | 0.66 | 1 | 3.70 (0.994) | 5.60 |
| | 1.06 | 3 | 6.11[e] (0.999)[e] | 5.76[e] |
| | 1.32 | 1 | 7.22 (0.998) | 5.46 |

[a] Average $k_2$ (25 °C) = 3.30 L mol$^{-1}$ s$^{-1}$; $k_2$ (30 °C) = 3.53 L mol$^{-1}$ s$^{-1}$; $k_2$ (40 °C) = 4.60 L mol$^{-1}$ s$^{-1}$; $k_2$ (50 °C) = 5.70 L mol$^{-1}$ s$^{-1}$ used for calculation of activation parameters. [b] Concentration of pyridinium salt = $6.597 \times 10^{-5}$ M. [c] Values of $k_{obsd}$ used in a plot of $k_{obsd}$ vs. [Nu] to give $k_2$ = 3.48 L mol$^{-1}$ s$^{-1}$. [d] Values of $k_{obsd}$ used in a plot of $k_{obsd}$ vs. [Nu] to give $k_2$ = 5.45 L mol$^{-1}$ s$^{-1}$. [e] Average values of the runs.

**Rate Variation with N Substituent Transferred.** Table III gives the rates for a series of N-para-substituted benzylpyridiniums. All the substituted compounds react faster than the parent: for the Cl, Me, and OMe substituents (**1b–d**), the increase is modest,

---

[*] To whom correspondence should be addressed at the University of Florida.

[†] In a preliminary communication[1] we referred to this mechanism as $S_{RN}2$. However, this symbol was used in a paper that appeared after submission but before publication of our manuscript by Galli and Bunnett (*J. Am. Chem. Soc.* **1979**, *101*, 6139) in a different way, and we therefore discontinue its use for our reaction to avoid confusion.

0002-7863/83/1505-0090$01.50/0

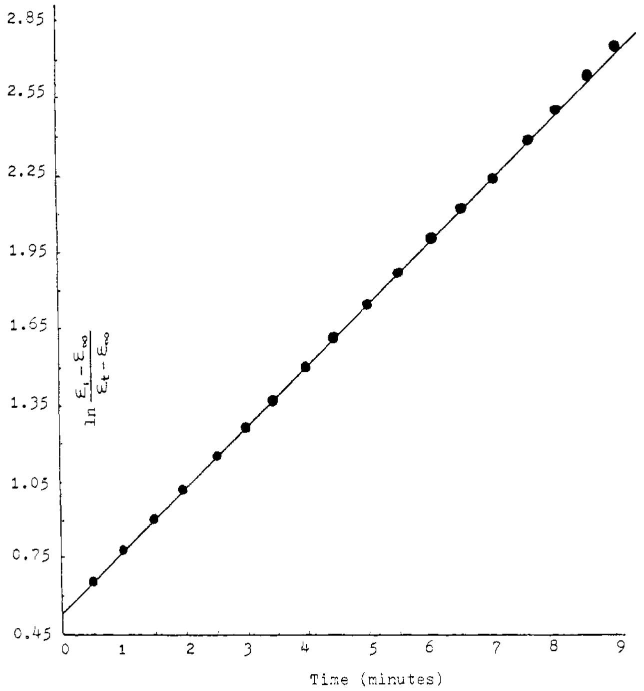


**Figure 1.** Dependence of $\ln (\epsilon_1 - \epsilon_\infty)/(\epsilon_t - \epsilon_\infty)$ on time for a typical reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate with sodium 2-nitropropanide in $Me_2SO$ at 25 °C.

Table II. Reaction of 1-Benzyl-2,4,6-triphenylpyridinium Tetrafluoroborate[a] with Sodium Nitrocyclohexanide in $Me_2SO$ at 25 °C ($\lambda$ = 312 nm)

| [Nu], $10^3$ M | $k_{obsd}$, $10^3$ $s^{-1}$ | $k_2$, L $mol^{-1}$ $s^{-1}$ ($r$) |
|---|---|---|
| 0.330 | 1.830 | 5.548 (0.999) |
| 0.495 | 2.644 | 5.344 (0.999) |
| 0.660 | 3.645 | 5.525 (0.997) |
| 0.825 | 4.479 | 5.432 (0.999) |
| 0.990 | 4.502 | 4.550 (0.996) |
| 1.155 | 6.016 | 5.211 (0.994) |
| 1.320 | 6.344 | 4.808 (0.997) |
| 1.650 | 9.622 | 5.834 (0.992) |
|  |  | av 5.247 |

[a] Concentration of pyridinium salt = 6.597 × $10^{-5}$ M.

Table III. Second-Order Rate Constants of 1-Substituted-2,4,6-triphenylpyridinium Tetrafluoroborates[a] with Sodium 2-Nitropropanide[b] in $Me_2SO$ at 25 °C

| 1-substituent | $k_{obsd}$, $10^3$ $s^{-1}$ ($r$)[c] | no. of runs | $k_2$, L $mol^{-1}$ $s^{-1}$ | analytical $\lambda$, nm |
|---|---|---|---|---|
| $Ph-CH_2-$ | 3.48 (0.996) | 3 | 3.30 | 312 |
| $p$-$ClPh-CH_2-$ | 6.17 (0.997) | 3 | 5.84 | 312 |
| $p$-$MePh-CH_2-$ | 4.31 (0.999) | 3 | 4.08 | 312 |
| $p$-$OMePh-CH_2-$ | 4.41 (0.995) | 3 | 4.17 | 312 |
| $p$-$NO_2Ph-CH_2-$ | $d$ | 6 | 12.4[e] | 312 |
| $Me_2CH-$ | 1.98 (0.992) | 3 | 1.88 | 308 |

[a] Concentration of pyridinium salt = 6.597 × $10^{-5}$ M. [b] Concentration of nucleophile = 1.056 × $10^{-3}$ M. [c] $r$ = correlation coefficient (ca. 10 points). [d] $k_{obsd}$ 9.77 $s^{-1}$ ($r$ = 0.99) at nucleophile = 0.792 × $10^{-3}$ M, $k_{obsd}$ 6.45 $s^{-1}$ ($r$ = 0.998) at 0.528 × $10^{-3}$ M, and $k_{obsd}$ 3.22 $s^{-1}$ ($r$ = 0.999) at 0.264 × $10^{-3}$ M. [e] Value obtained from the plot of $k_{obsd}$ vs. $[Nu^-]$.

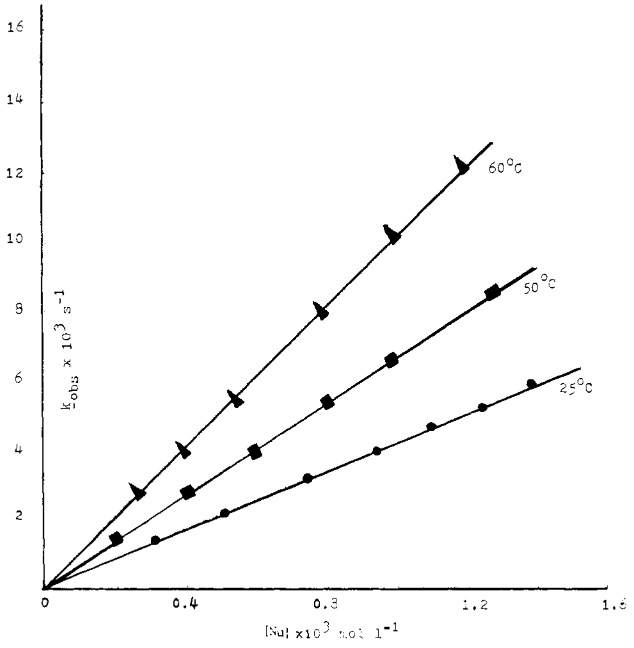


**Figure 2.** Dependence of $k_{obsd}$ on nucleophile concentration for the reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate with sodium 2-nitropropanide in $Me_2SO$ at 25, 50, and 60 °C.

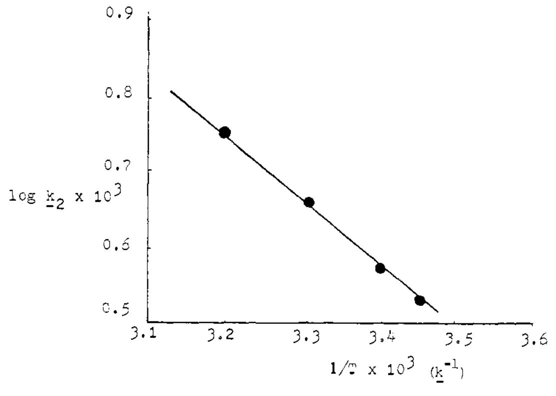


**Figure 3.** Arrhenius plot for the reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate with sodium 2-nitropropanide in $Me_2SO$.

Table IV. Rate Constants for the Reaction of 1-Alkyl-2,4,6-triphenylpyridinium Tetrafluoroborates[a] with Sodium 2-Nitropropanide in $Me_2SO$ at 25 °C (CTC Formation) and 100 °C (Product Formation) (Measured at 308 nm)

| 1-substituent | range of $[^-CMe_2NO_2]$, $10^3$ M | $k_\alpha$[b] at 25 °C, L $mol^{-1}$ $s^{-1}$ | $k_2$[c] at 100 °C, L $mol^{-1}$ $s^{-1}$ |
|---|---|---|---|
| Me | 0.33-1.58 | 2.52 ± 0.07 | 0.22 ± 0.01 |
| $n$-butyl | 0.33-1.84 | 1.79 ± 0.07 | 0.28 ± 0.01 |
| neopentyl | 0.33-1.58 | 1.54 ± 0.04 | 0.27 ± 0.01 |

[a] Concentration of pyridinium salt = 6.597 × $10^{-5}$ M. [b] Rate of formation of CTC. [c] Rate of formation of pyridine product.

but the rate became unusually fast for the $p$-nitro compound (**1e**). Note that, as is discussed later, the 4-OMe compound (**1d**) gave preparatively 4-anisaldehyde and that the reaction thus takes a different course here.

Table III also gives the rate data for the $N$-isopropyl compound (**1h**): the second-order rate constant is ca. half that of the $N$-benzyl compound.

For the $N$-(primary alkyl) substituents, methyl (**1f**) and $n$-butyl (**1g**), bimolecular kinetics are observed at 25 °C with $k_2 \simeq 2$ L

---

(1) For a preliminary communication of part of this work, see: Katritzky, A. R.; de Ville, G.; Patel, R. C. *Tetrahedron Lett.* **1980**, 1723.

(2) Katritzky, A. R.; de Ville, G.; Patel, R. C. *J. Chem. Soc., Chem. Commun.* **1979**, 602; *Tetrahedron* **1980**, *36*, 679; *Ibid.* **1981**, *37*, 25.

(3) Katritzky, A. R.; Manzo, R.; Lloyd, J. M.; Patel, R. C. *Angew. Chem.* **1980**, *92*, 306. Katritzky, A. R. *Tetrahedron* **1980**, *36*, 679 and references therein.

(4) Hass, H. B.; Bender, M. L. *J. Am. Chem. Soc.* **1949**, *71*, 1767.

Chart I

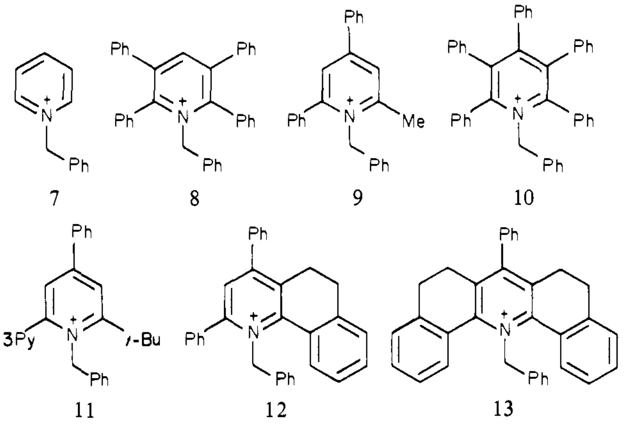


Table V. Second-Order Rate Constants for the Reaction of 1-Benzyl-2,4-diphenyl-5,6-dihydrobenzo[*h*]quinolinium Tetrafluoroborate[a] (12) with Sodium 2-Nitropropanide in $Me_2SO$ at 30 °C

| $[Nu^-]$, $10^3$ M | $k_{obsd}$, $10^3$ $s^{-1}$ (*r*) | $k_2$, L $mol^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.3299 | 0.0169 (0.9994) | 0.0512 |
| 0.6597 | 0.0391 (0.9997) | 0.0593 |
| 0.9896 | 0.0547 (0.9999) | 0.0553 |
| 1.319 | 0.0656 (0.9998) | 0.0497 |
| 1.649 | 0.0869 (0.9999) | 0.0527 |

[a] Concentration = $6.597 \times 10^{-5}$ M, kinetic wavelength 322 nm.

$mol^{-1}$ $s^{-1}$, cf. *N*-benzyl $k_2 \simeq 3.3$ L $mol^{-1}$ $s^{-1}$ (Table IV). However, after several days, the spectrum still does not correspond to that of 2,4,6-triphenylpyridine: the pyridinium absorption maximum at $\lambda = 308$ falls (from $\epsilon = 27000$ to $\epsilon = 15000$) and the appearance of a band of low $\epsilon$ (ca. 1300 assuming 100% conversion) at $\lambda = 425$ nm is seen. If now the temperature is raised to 100 °C, still following the same absorption maximum, second-order kinetics are observed for the formation of pyridine (Tables B and IV). (Table B is in the supplementary material.) Clearly, at 25 °C an equilibrium is established with an intermediate that at 100 °C is decomposing to the products.

**Dependence of Rate on Leaving Group.** The effect of changing the pyridinium leaving group on the rate was measured qualitatively by carrying out preparatively the reaction of various pyridiniums all containing the *N*-benzyl group with sodium 2-nitropropanide and determining the yield of 2-benzyl-2-nitropropane formed.

The parent 1-benzylpyridinium (**7**) gave no product, and even the 2,3,5,6-tetraphenyl derivative (**8**) with an unblocked 4-position gave only 14% yield, possibly due to the easy formation of an adduct (Chart I). Substitution of a methyl substituent for a 2-phenyl group as in **9** gives none of the expected product, possibly because of proton abstraction from the methyl. However, the extra phenyl substituents in the pentaphenyl compound (**10**) or the replacement of the 2,6-phenyl groups by *tert*-butyl and 3-picolyl (**11**), while they appeared to slow the reaction markedly, had little effect on the product yield (56% and 64%, respectively).

Holding the 2- (**12**) or 2- and 6-phenyl rings (**13**) in conjugation with the pyridinium ring slows down the reaction considerably. These reactions with sodium 2-nitropropanide were followed spectrophotometrically at $\lambda = 322$ and 325 nm, respectively, (Table V). Compound **12** reacted very slowly at 30 °C in bimolecular kinetics to give $k_2 = 0.05$ L $m^{-1}$ $s^{-1}$, cf. $k_2 = 3.52$ L $mol^{-1}$ $s^{-1}$ for 2,4,6-triphenylpyridinium (**4**). Compound **13** failed to show any reaction and was recovered unchanged in a preparative reaction.

**Reaction with Sodium Nitromethanide.** Addition of sodium nitromethanide to 1-benzyl-2,4,6-triphenylpyridinium leads to an immediate decrease of the absorbance at $\epsilon$ 312 from $\epsilon = 34000$ to $\epsilon = 3000$ (assuming 100% conversion). Subsequently, at a first-order rate the appearance (Figure 4) of a 2,4,6-triphenylpyridine (**4**) can be followed at 312 ($\epsilon = 8000$). Table VI reports the variation of $k_{obsd}$ with [pyridinium] and $[CH_2NO_2^-]$.

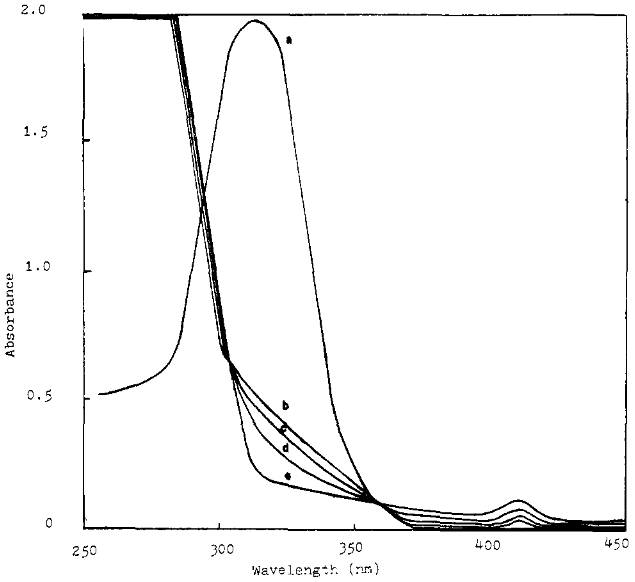


Figure 4. UV-visible spectral changes during the reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate with sodium nitromethanide in $Me_2SO$ at 25 °C. [Concentration of pyridinium salt = $6.597 \times 10^{-5}$ $mL^{-1}$. Concentration of sodium nitromethanide = $1.056 \times 10^{-3}$ $mL^{-1}$]. (a) Absorption for the pyridinium salt without sodium nitromethanide; (b) absorption on immediate mixing of the pyridinium salt and sodium nitromethanide solution; (c–e) absorptions of the reaction mixture after successive 0.5-h time intervals.

Table VI. First-Order Rate Constants of 1-Benzyl-2,4,6-Triphenylpyridinium[a] Tetrafluoroborate with Sodium Nitromethanide in $Me_2SO$ at 25 °C

| $[Pyr^+]$, $10^5$ M | $[Nu^-]$, $10^3$ M | $k_{obsd}$, $10^4$ $s^{-1}$ (*r*) |
|---|---|---|
| 6.597 | 0.3299 | 5.71 (0.9994) |
| 6.597 | 0.6597 | 6.11 (0.9994) |
| 6.597 | 0.9896 | 5.83 (0.9998) |
| 6.597 | 1.319 | 5.67 (0.9989) |
| 3.299 | 1.319 | 5.90 (0.9997) |
| 8.246 | 1.319 | 5.81 (0.9991) |
| av. $k_{obsd} = k_1 = 5.84 \times 10^{-4}$ $s^{-1}$ | | |

[a] Kinetic wavelength 312 nm.

We concluded that, just as in the reaction of the *N*-alkylpyridiniums with 2-nitropropanide, reaction of the benzylpyridinium and nitromethanide to give an intermediate is essentially complete and that this reacts further with relatively slow break down to products.

**Proposed Mechanism.** The observation of *N*-benzyl transference from *N*-benzyl-2,4,6-triphenylpyridiniums in $Me_2SO$ to 2-nitropropanide in clean bimolecular kinetics led us to propose[1] a novel mechanism. This was originally[1] termed $S_{RN}2$ (substitution radical nucleophile bimolecular), but this designation is now inappropriate (see footnote to abstract). The reaction gives nucleophilic substitution products; the fast rates are consistent with electron-transfer catalysis as defined by Alder[5] and Eberson[6] and clean kinetics infer 1:1 association between substrate and nucleophile. What we now term the "nonchain radicaloid" mechanism involves the intermediate formation of a charge-transfer complex (CTC) between the pyridinium and nitronate in an equilibrium $\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{3}$: the CTC then decomposes to give the radical of the N-substituent **5** and the pyridine (**4**). Combination of this radical with $\dot{C}Me_2NO_2$ gives the C-alkylated product (Scheme I). This mechanism is distinct from the well-established $S_{RN}1$[7] chain

---

(5) Alder, R. A. *J. Chem. Soc., Commun.* **1980**, 1184.

(6) Eberson, L.; Jünsson, L. *J. Chem. Soc., Chem. Commun.* **1980**, 1187.

(7) (a) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463, 7464. (b) For a summary, see: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734 and references therein.

pathway in that the clean bimolecular kinetics indicate a nonchain (probably solvent cage trapped) process. In the following sections, evidence is presented in favor of the nonchain radicaloid mechanism.

## Discussion

**Evidence in Favor of a Free Radical Reaction Mechanism. (1) Structure of Products.** Preparative reactions give C-alkylation for each of nitromethanide (**2a**), nitroethanide (**2b**), and nitropropanide (**2c**), whether the group transferred is primary alkyl, secondary alkyl, or aralkyl.[2] Significantly, the *N*-neopentyl substituent in **1j** is transferred (at rates similar to those for the *N*-methyl and *N*-*n*-butyl analogues) to give the 2,4,4-trimethyl-2-nitropentane (50%)—a result that does not favor an $S_N2$ reaction path.

Previously, preparative reactions with nitromethanide (**2a**) were reported to proceed in refluxing ethanol with the isolation of good yields of benzyl-transferred C-alkylated products.[2] We now find that although the reaction between **1a** and **2a** in $Me_2SO$ at 25 °C in air gives only a low yield of 2-phenylnitroethane, when carried out under $N_2$ the reaction gave 58% of the distilled product; as mentioned above, both the reagent and product are sensitive to air oxidation in basic media.

The two modes of attack by sodium 2-nitropropanide on *p*-nitrobenzyl compounds with moderate leaving groups (e.g., chloride or trimethylamine) are well established: O-alkylation is a result of $S_N2$ (relatively slow) attack whereas the much faster C-alkylation is due to the intermediacy of free radicals.[7b] In our reactions the predominant C-alkylation and the formation of an unrearranged product in the neopentyl (**1j**) case strongly point to a radical pathway.

**(2) Dependence of Kinetic Rates on Structure of N Substituent.** With the leaving pyridine group constant, the second-order rate constants for[8] $S_N2$ reactions of type **14** + **15** → **16** + **17** decrease sharply depending on the N substituent transferred in the order R = benzyl > methyl > *n*-alkyl, secondary alkyl, as is expected for $S_N2$ reactions. By contrast, we now find for reactions of nitropropanide (**2c**) with the *N*-benzyl derivative (**1a**) and with the isopropyl analogue (**1h**) similar $k_2$ values, both of which are far larger than the $k_2$ value for the *N*-*n*-alkyl analogues methyl and *n*-butyl (see also section 6 below). This behavior is to be expected for a radical mechanism; benzyl and secondary alkyl radicals are both more stable than primary alkyl.

The reaction of *N*-*n*-alkyl compounds **1f** and **1g** at 25 °C strongly supports formation of an intermediate: the observation of a band in the UV at λ 425 nm ($\epsilon \sim 1300$) is consistent with a charge-transfer complex. The data of Table C (supplementary material) and Table IV, together with observed UV spectra, allow the calculation of $K = k_\alpha/k_\beta$ for this equilibrium from eq 4, which is itself derived from eq 1–3.

$$K = \frac{[\mathrm{CTC}]}{[\mathrm{Py}^+][^-\mathrm{CMe_2NO_2}]_0} = \frac{[\mathrm{Py}^+]_0 - [\mathrm{Py}^+]}{[\mathrm{Py}^+][^-\mathrm{CMe_2NO_2}]_0} = \frac{1}{[^-\mathrm{CMe_2NO_2}]_0}\left\{\frac{[\mathrm{Py}^+]_0}{[\mathrm{Py}^+]} - 1\right\} \quad (1)$$

$$A_e = \epsilon_e[\mathrm{Py}^+]_0 = \epsilon_{\mathrm{CTC}}\{[\mathrm{Py}^+]_0 - [\mathrm{Py}^+]\} + \epsilon_{\mathrm{py}}[\mathrm{Py}^+] \quad (2)$$

$$\frac{[\mathrm{Py}^+]_0}{[\mathrm{Py}^+]} = \frac{\epsilon_{\mathrm{py}} - \epsilon_{\mathrm{CTC}}}{\epsilon_e - \epsilon_{\mathrm{CTC}}} \quad (3)$$

$$K = \frac{1}{[^-\mathrm{CMe_2NO_2}]_0}\left\{\frac{\epsilon_{\mathrm{py}} - \epsilon_e}{\epsilon_e - \epsilon_{\mathrm{CTC}}}\right\} \quad (4)$$

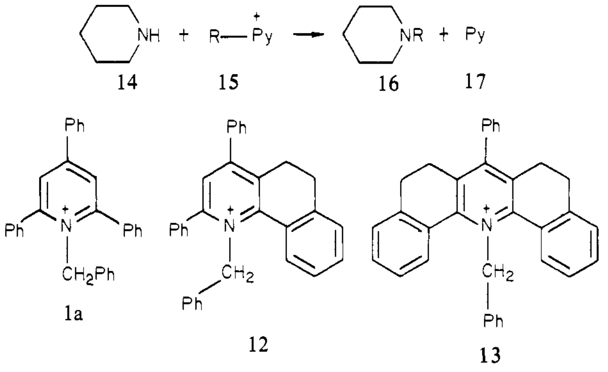
In these equations, $\mathrm{Py}^+$ is the pyridinium, and $\epsilon_{\mathrm{py}}$, $\epsilon_{\mathrm{CTC}}$, and $\epsilon_e$ are the exinction coefficient of the pyridinium, charge-transfer complex, and equilibrium mixture, respectively.

Table VII. Second-Order Rate Constants for Displacement Reactions of 1a

| | benzyl para substituent | | | | |
|---|---|---|---|---|---|
| | OMe | Me | H | Cl | $NO_2$ |
| $k_2 \times 10^3$ [a] | 18.0[b] | 8.52 | 4.95 | 5.88 | 2.96 |
| $k_2$ [c] | 4.17[d] | 4.08 | 3.30 | 5.84 | 12.4 |

[a] For reaction with piperidine in chlorobenzene solution at 100 °C in L $mol^{-1}$ $s^{-1}$ (ref 9). [b] Second-order rate at 100 °C extrapolated from rate measured at lower temperatures. [c] For reaction with $^-CMe_2NO_2$ in $Me_2SO$ solution at 25 °C in L $mol^{-1}$ $s^{-1}$. [d] Rate for O-alkylation; rate for C-alkylation must be significantly slower.

Scheme II



| | 1a | 12 | 13 |
|---|---|---|---|
| $S_N2$ | 1 | 60 | 900 |
| radicaloid | 1 | 0.015 | 0.0 |

Using a large excess of nucleophile, we find the following values for $\epsilon_{\mathrm{CTC}}$: *N*-methyl, 15 000; *N*-*n*-butyl, 14 900; *N*-neopentyl, 14 800. This gives the following values for *K* and (using $k_\alpha$ from Table IV) for $k_\beta$ at 25 °C:

| N substituent | methyl | *n*-butyl | neopentyl |
|---|---|---|---|
| *K*, L $mol^{-1}$ | 5090 ± 530 | 5870 ± 600 | 6040 ± 170 |
| $k_\beta$, $s^{-1}$ | $0.49 \times 10^{-3}$ | $0.30 \times 10^{-3}$ | $0.25 \times 10^{-3}$ |

The effect on the rate constant of para substituents in the benzyl group in **1a–e** in our nonchain radicaloid reactions is quite different from that found for the regular $S_N2$ reactions with piperidine. The different behavior patterns are contrasted in Table VII. The $S_N2$ reaction shows the expected rate enhancement by electron-donor substituents and rate decrease for a nitro substituent.[9] For the reaction with $\dot{C}Me_2NO_2$, all substituents increase the rate, particularly *p*-$NO_2$; this is as expected for the stabilization of benzyl radicals.[7b] It is particularly noteworthy that the *p*-nitrobenzyl derivative does not react by the $S_{RN}1$ chain mechanism.

In the *p*-methoxybenzyl case, O-alkylation in $Me_2SO$ evidently successfully competes with C-alkylation of the 2-nitropropanide to give the aldehyde: this substrate is known to undergo very fast $S_N1$ ionic dissociation,[9] and the *p*-methoxybenzyl carbonium ion probably *O*-alkylates the 2-nitropropanide.

**(3) Dependence of Kinetic Rates on Structure of the Leaving Group.** The second-order rate constants of $S_N2$ displacement reactions of type **14** + **15** → **16** + **17** where the leaving group Py is a substituted pyridine[8] depend markedly on the structure of Py (Scheme II). Rate ratios for **1a**:**12**:**13** are ca. 1:60:900; this can be understood in terms of steric acceleration in **12** and especially **13** because of relief of steric strain in the transition state.

In complete contrast, the reaction of **12** with $\dot{C}Me_2NO_2$ to give $PhCH_2CMe_2NO_2$ ($k_2 = 0.05$ L $mol^{-1}$ $s^{-1}$) is far slower (66×) than that of **1a** ($k_2 = 3.5$ L $mol^{-1}$ $s^{-1}$), and no product at all was obtained from **13**. We believe that this is due (a) to reduced ease of one-electron reduction in **12** and **13** and (b) particularly to enhanced stability of radical intermediates derived from **12** and especially **13**[10] (see section 7 on radical-decay half-lives).

---

[8] (a) Katritzky, A. R.; Musumarra, G.; Sakizadeh, K.; El-Shafie, S. M. M.; Jovanovic, B. *Tetrahedron Lett.* **1980**, 2697. (b) Katritzky, A. R.; Musumarra, G.; Sakizadeh, K. *Ibid.* **1980**, 2701.

[9] Katritzky, A. R.; Musumarra, G.; Sakizadeh, K. *J. Org. Chem.* **1981**, *46*, 3831.

Table VIII. Reaction of 1-Benzyl-2,4,6-triphenylpyridinium Tetrafluoroborate with Sodium 2-Nitropropanide and Piperidine

| reaction type | nucleophile | solvent | temp, °C | $k_2$, L mol$^{-1}$ s$^{-1}$ | $\Delta S^{\ddagger}$, cal mol$^{-1}$ s$^{-1}$ | $E_a$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|
| nonchain radicaloid | $^{-}CMe_2NO_2$ | $Me_2SO$ | 25 | 3.3 | −58 ± 2 | 4.3 ± 0.6 |
| $S_N2$ | $C_5H_{10}NH$ | $PhCl^a$ | 100 | $4.94 \times 10^{-3}$ | −26 ± 2 | 17.0 ± 1.0 |
| | | $Me_2SO^b$ | 100 | $3.62 \times 10^{-3}$ | | |

[a] Reference 9. [b] Katritzky, A. R.; Musumarra, G.; Sakizadeh, K.; Misic-Vukovic, M. S. *J. Org. Chem.* 1981, *46*, 3820.

**(4) Dependence of Kinetic Rates on Structure of the Nucleophile.** Second-order rate constants for the $S_N2$ reaction of type **14** + **15** → **16** + **17** are subject to conventional steric hindrance in the nucleophile: thus rates for 2-picoline[11] are less than those for pyridine by a factor of ~4.

The effects of nucleophilic size in the presently reported nonchain radicaloid rates are considerably more complex. Steric hindrance in the formation of the charge-transfer complex (CTC) from **1** and **2** should depend on the size of the nitronate anion because close encounter is involved (Scheme I). In agreement, we find that on addition of nitromethanide **2a** there is an immediate decrease of the absorbance of **1a** at $\lambda = 312$ nm going to the charge-transfer complex (CTC); subsequently, at a first-order rate the appearance of **4** is followed at 312 nm. By contrast, in the reaction of **1a** with the large 2-nitropropanide **2c**, only a small equilibrium concentration of the CTC is formed and the formation of product follows second-order kinetics in **1a** and **2c**. For *N*-alkyl (**1**) salts, this equilibrium with nitropropanide **2c** is measurable at 25 °C and is discussed above.

**(5) Absolute Comparisons of Kinetic Rates and Activation Parameters.** For the *N*-benzyl compound **1a**, the absolute rate of reaction with 2-nitropropanide (**2c**) is much greater (1000× at a lower temperature) than that for **1a** with piperidine (cf. Table VIII).

The reaction of 1-benzyl-2,4,6-triphenylpyridinium with sodium 2-nitropropanide (**2c**) has a low Arrhenius energy and a large negative entropy of activation. Such activation parameters, cf. decomposition of phenyldiimide,[12] are consistent with a reaction involving free radicals (small $E_a$[13]) and a highly organized transition state (i.e., a large negative $\Delta S^{\ddagger}$). Contrast the values for the reaction with piperidine (cf. Table VIII).

**(6) Evidence for Radical Intermediates from $^1H$ NMR and ESR Studies.** When *N*-methylpyridinium (**1f**) is mixed with $^{-}CMe_2NO_2$ in $Me_2SO\text{-}d_6$ at 25 °C and examined by $^1H$ NMR, very rapid broadening of the signals of **1f** at $\delta$ 7.3–8.2 is observed: the broadened spectra are stable for 2 days. At 100 °C the broadened signals collapse slowly followed by the emergence of sharp signals for 2,4,6-triphenylpyridine after ca. 2 h.

The same mixture of 25 °C, rapidly cooled in the liquid $N_2$, shows a simple ESR signal centered at $g = 2.0013$, consistent for molecular complexes.[14]

A similar experiment with the *N*-benzylpyridinium showed no broadening in $^1H$ NMR (pyridinium signals gradually disappear at 25 °C, being replaced by those of the pyridine) and no ESR signal.

Thus the *N*-methyl compound forms an equilibrium amount of CTC detectable by $^1H$ NMR and ESR, whereas from *N*-benzyl a small concentration of the CTC decays to products. These results are consistent with the kinetic data from UV studies.

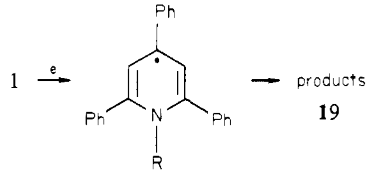
**(7) Electrochemical Studies and Radical-Decay Half-Lives.** Electrochemical studies[10] on a series of pyridinium salts have shown that (a) they are readily reduced in two reversible one-electron steps with $E_{1/2}(1) = -700$ to $-880$ mV and (b) $E_{1/2}(2) = -1170$ to $-1500$ mV. Using $E_{1/2}(1) = -0.79$ V for *N*-benzyl-2,4,6-triphenylpyridinium and $E_{1/2} = +0.59$ V for sodium 2-nitropropanide,[10] we calculated $\Delta G$ to be +4.7 kcal mol$^{-1}$. This low energy explains the nonsensitivity toward stimulation by light in our reaction; i.e., the reaction proceeds spontaneously.

Table IX. Radical Decay Half-Lives[20] from Cyclic Voltammetry of *N*-Substituted-2,4,6-triphenylpyridinium Cations

| N substituent | $E_{1/2}(1)$,[a] mv | $E_{1/2}(2)$,[a] mv | $t_{1/2}$,[a] s |
|---|---|---|---|
| $-CH_2Ph$ | −791 | −1412 | <0.01 |
| $-CH_2(CH_2)_2CH_3$ | −722 | −1278 | 1800[b] |
| $-CH(CH_3)_2$ | −744 | −1212 | 5 |
| $-Ph$ | −690 | −851 | >1000 |

[a] In $Me_2SO$. [b] By electrochemical generation of radical and recording of its UV spectrum with time: ref 10.

The reaction sequence **1** → **18** → **19** was followed by cyclic voltammetry.[10] The half-lives of the radical intermediates **18**



18

at 25 °C depend markedly on the N substituent (Table IX). The faster nonchain radicaloid rates found for **1a** (R = $CH_2Ph$) and **1h** (R = *i*-Pr) compared with that for **1g** (R = *n*-Bu) with the lack of reaction found for **1i** (R = Ph) with $\dot{C}Me_2NO_2$ are in line with these results.

**Evidence against a Chain Reaction Mechanism. (1) Kinetic Dependence Expected for a Radical Chain Reaction.** As Bunnett wrote[15] "The overall rate law for a radical chain reaction is composite, being determined by the rate laws that govern initiation, termination and the propagation steps that are kinetically crucial by virtue of the termination steps that prevail".[16,17] Kinetic complexities of chain reactions have been commented on by Ingold[18] and Hine.[19] The $S_{RN}1$ mechanism leads to complex kinetics;[20] one rate was "approximately proportional to 0.84 power of light intensity" and "quantum yields are about the 1.12 power of nucleophile".[15] Zero-order behavior in substrate (iodobenzene) was found.[21] In competition experiments with diethyl phosphite anion, iodobenzene reacts about 1000 times faster than bromobenzene, but only 8 times faster in individual photostimulated reactions with acetone enolate.[22] For a thermal $S_{RN}1$ reaction, "the (kinetic) data obtained do not fit the simple rate laws appropriate for first- or second-order kinetics or for reaction zero order in reactants but inverse first order in a product".[23]

**(2) Kinetic Dependence Expected for Radical Nonchain Mechanisms.** Simple rate laws are expected. Some examples are

---

(10) Katritzky, A. R.; de Ville, G.; Patel, R. C.; Lunt, E., manuscript in preparation.

(11) Katritzky, A. R.; Jovanovic, B., recent results.

(12) Huang, P. C.; Kosower, E. M. *J. Am. Chem. Soc.* **1967**, *89*, 3910.

(13) Cf.: Walling, C. "Free Radicals in Solution"; Wiley: New York, 1959; p 39.

(14) Matsunaga, Y. *J. Chem. Phys.* **1959**, *30*, 855.

(15) Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690.

(16) Huyser, E. S. "Free Radical Chain Reactions"; Wiley-interscience: New York, 1970; p 44.

(17) Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions", 3rd ed., Part 1; Lewis, E. S., Ed.; Wiley: New York, 1974: p 381 (vol. 6 of series "Techniques of Chemistry"; E. S., Lewis, Ed).

(18) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, New York, 1969; pp 602–610, 1044–1064.

(19) Hine, J. "Physical Organic Chemistry"; 2nd ed.; McGraw Hill: New York, 1962, pp 424–438.

(20) Beletskaya, I. P.; Drozd, V. N. *Russ. Chem. Rev.* (*Engl. Transl.*) **1979**, 431–448 (see especially p 446).

(21) Bunnett, J. F.; Scamehorn, R. G.; Traber, R. P. *J. Org. Chem.* **1976**, *41*, 3677.

(22) Bunnett, J. F.; Traber, R. P. *J. Org. Chem.* **1978**, *43*, 1867.

(23) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.

known: the decomposition of phenyldiimide[12] PhN:NH → PhH + $N_2$ is bimolecular with $\Delta G^{\ddagger} = 9$ kcal mol$^{-1}$, $\Delta S^{\ddagger} = -23$ eu, and is considered to involve the radical cage mechanism

$$2PhN{:}NH \rightarrow [PhNNH_2{\cdot}PhN{:}N] \rightarrow PhH + N_2 + PhN{:}NH$$

The radical reactions of triphenylmethyl dimer with iodine and NO are first-order processes controlled by dissociation of the dimer.[24]

**(3) Effect of Initiators and Inhibitors.**[25] The rates of many $S_{RN}1$ reactions are much increased by light,[26] which acts as an initiator with quantum yields of up to 6000.[27] $S_{RN}1$ rates are much reduced by certain inhibitors: cupric salts,[28] *m*- and *p*-dinitrobenzene,[29] oxygen,[25,26,30] and di-*tert*-butyl nitroxide.[31]

By contrast, nonchain radical reactions should be much less susceptible to initiators and inhibitors in small quantities. The nonsensitivity of reactions of *m*-nitrocumyl chloride[32] to oxygen originally led Kornblum to propose[25] that these proceeded by a nonchain radical process, although this suggestion has not been followed up in his later papers.

In our reactions, specifically that of 1-benzyl-2,4,6-triphenylpyridinium with $\bar{C}Me_2NO_2$ in $Me_2SO$, we have not found any sensitivity to light or to small quantities (up to 25 mol %) of *m*-dinitrobenzene. This is due presumably to the reduction potential of the pyridiniums, compare $E_{1/2}$(pyridinium) = −0.79 V with $E_{1/2}$(*m*DNB) = −0.52 V.

**(4) Mutual Relationship of Chain $S_{RN}1$ and Nonchain Radicaloid Processes.** Clearly, successive reduction of the chain length leads in the limit, at chain length unity, to a nonchain process. Hence, our nonchain radicaloid mechanism is, in one sense, a limiting case of the $S_{RN}1$ mechanism.

In $Me_2SO$ the reaction of 1-benzyl-2,4,6-triphenylpyridinium with sodium 2-nitropropanide follows second-order kinetics below 50 °C. However, above 60 °C the reaction is very fast, and the rate is not practically measurable; probably a chain reaction now intervenes, perhaps because of breakup of the solvent cages.

Kornblum initially proposed[33] a nonchain process for this carbon alkylation by *p*-nitrobenzyl halides but later revised the mechanisms to a radical chain.[7b] It is conceivable that a reaction could proceed by a radical chain *or* a radical nonchain process depending on the conditions.

**Alternative Explanations to the Reported Observations.** We have considered several alternative explanations to the reported observations and, at the suggestion of the referees, briefly mention some of them here.

**(1) Long-Chain Sequence.** Under certain conditions, it is theoretically possible for a chain sequence to show simple kinetics. The sequence could be $RPy{\cdot} + R'_2CNO_2^- \rightarrow Py + RR'_2CNO_2^{-}{\cdot}$ followed by $RR'_2CNO_2^{-}{\cdot} + RPy^+ \rightarrow RR'_2CNO_2 + RPy{\cdot}$. If now the rate of initiation were $k_2[RPy^+][R'_2CNO_2^-]$ and of termination of $RPy{\cdot} + A^- \rightarrow$ nonradical species, then for long chains, $-d[R'_2CNO_2^-]/dt = k[RPy^+][R'_2CNO_2^-]$.

However, the insensitivity of the rates to inhibition and initiation make a long-chain process unlikely. Moreover, there are few examples of such clean initiation with termination steps resulting in simple kinetics for chain reactions.

**(2) Formation of an α-Adduct and Electrocyclic Reaction.** If the nitronate anion originally added to the pyridinium to form an O-linked adduct at the α position, this could give the products by an electrocyclic reaction. There are several arguments against such an interpretation: (a) Pyridiniums normally add nitronate anions to the γ position to form C–C bonds.[34]

(b) Such a rearrangement would involve retention at the α-carbon atom of the *N*-alkyl group, which is unfavorable on orbital grounds.

(c) The complex formed in some cases does not show the expected NMR signals for such an adduct.

(d) The pattern of changes of rate of the reaction with change of α substituent in the pyridinium does not support such a mechanism.[35]

## Experimenal Section

Melting points were recorded on a Reichert hot stage microscope and are uncorrected. UV spectra of reactants and products ($6.597 \times 10^{-5}$ M) in $Me_2SO$ were run on a Pye Unicam SP 800A spectrophotometer. For the rate measurements, Pye Unicam SP8-200 (temperature programmable) and Pye Unicam SP6-500 instruments were used. Analar $Me_2SO$ (BDH or Aldrich) was used for the kinetic runs.

**1-Substituted-2,4,6-triphenylpyridinium tetrafluoroborates** were made following literature methods from 2,4,6-triphenylpyrylium tetrafluoroborate[36] and the appropriate amine: 1-benzyl-, mp 193–195 °C (lit.[37] mp 196–197 °C); 1-(4-chlorobenzyl)-, mp 141–143 °C (lit.[38] mp 144 °C); 1-(4-methylbenzyl)-, mp 118–120 °C (lit.[39] mp 122 °C); 1-(4-methoxybenzyl)-, mp 146–147 °C (lit.[38] mp 148 °C); 1-(4-nitrobenzyl)-, as needles mp 132–134 °C (Calcd for $C_{30}H_{23}N_2O_2BF_4$: C, 67.9; H, 4.3; N, 5.2. Found: C, 67.3; H, 4.5; N, 5.1); 1-isopropyl-, mp 168–170 °C (lit.[40] mp 171–173 °C); 1-methyl-, mp 215–217 °C (lit[37] mp 217–218 °C); 1-*n*-butyl-, mp 201–203 °C (lit.[37] mp 201–202 °C); 1-(2-phenylethyl)-, mp 275–277 °C (lit.[37] mp 274 °C); 1-neopentyl-, mp 235 °C (lit.[41] mp 235 °C).

**Preparative Reactions of 1-Substituted-2,4,6-triphenylpyridinium Tetrafluoroborates (1) with Sodium 2-Nitropropanide in $Me_2SO$.** NaH (0.72 g, 0.03 mol) was dissolved in MeOH (10 mL), and 2-nitropropane (2.67 g, 0.03 mol) was added with stirring. MeOH was removed in vacuo (25 °C (0.5 mmHg)). To the residue were added 1-(4-nitrobenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate (5.30 g, 0.01 mmol) and $Me_2SO$ (30 mL) and the whole was heated at 80 °C for 2 h. When no further pyridinium remained, as shown by TLC (silica, $CH_2Cl_2$), the solution was cooled and the separated 2,4,6-triphenylpyridine filtered off. The filtrate was quenched with water (30 mL) and extracted with $Et_2O$ (3 × 25 mL) and the extract was dried over $MgSO_4$. Dry HCl was passed to remove residual 2,4,6-triphenylpyridine and the filtrate evaporated at 25 °C (15 mmHg) to give 2-(4-nitrobenzyl)-2-nitropropane as needles (80%), mp 65–66 °C (lit.[4] mp 64–66 °C).

The following reactions were carried out under similar conditions: 1-methyl-2,4,6-triphenylpyridinium tetrafluoroborate gave 2-methyl-2-nitropropane (57%), mp 26 °C (lit.[42] mp 25–26 °C). 1-(Neopentyl)-2,4.6-triphenylpyridinium (**1j**) gave 2,4,4-trimethyl-2-nitropentane (50%), bp 54 °C (3 mmHg) (Found: C, 60.32; H, 10.51; N, 8.78. $C_{18}H_{17}NO_2$ requires C, 60.37; H, 10.69; N, 8.80. $^1$H NMR ($CDCl_3$) δ 2.05 (s, 2 H), 1.70 (s, 6 H), 1.20 (s, 9 H). 1-(4-Methoxybenzyl)-2,4,6-triphenylpyridinium tetrafluoroborate gave 4-anisaldehyde (69%) as the DNP, mp 247–250 °C (lit.[43] mp 254 °C).

**Reaction of 1a with Sodium Nitromethanide.** Nitromethane (0.03 mol, 1.83 g) was added to a solution of sodium hydride (0.03 mol, 0.72 g) in methanol (3 mL), and the mixture was evaporated (25 °C, 1 mmHg) to give sodium nitromethanide. This was suspended in $Me_2SO$ (10 mL) with rapid stirring at 25 °C and flushed with $N_2$. A solution of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (0.01 mol, 4.85 g) in $Me_2SO$ (20 mL) was slowly added dropwise. Stirring was continued for

---

(24) Reference 18, pp 1232–1234.

(25) Kornblum, N.; Earl, G. W.; Holy, N. L.; Manthey, J. W.; Musser, M. T.; Snow, D. H.; Swiger, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 6221.

(26) Kornblum, N.; Stuchal, F. W. *J. Am. Chem. Soc.* **1970**, *90*, 1804.

(27) Wade, P. A. Ph.D. Thesis, Purdue, 1973 (quoted in ref 7b).

(28) Kornblum, N.; Michael, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5662.

(29) Kornblum, N.; Michael, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660.

(30) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 725.

(31) Pinnick, H. W. Ph.D. Thesis, Purdue, 1969 (quoted in ref 7b).

(32) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Manthey, J. W.; Musser, M. T.; Swiger, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 6219.

(33) Kerber, R. C.; Urry, G. W.; Kornblum, N. *J. Am. Chem. Soc.* **1965**, *87*, 4520.

(34) Damji, S. W. H.; Fyfe, C. A.; Smith, D.; Sharom, F. J. *J. Org. Chem.* **1979**, *44*, 1761.

(35) Unpublished work from this laboratory.

(36) Lombard, R.; Stêphan, J.-P. *Bull. Soc. Chim. Fr.* **1958**, 1458.

(37) Katritzky, A. R.; Gruntz, U.; Kenny, D. H.; Rezende, M. C.; Sheikh, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 430.

(38) Katritzky, A. R.; Gruntz, U.; Ikizler, A. A.; Kenny, D. H.; Leddy, B. P. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 439.

(39) Katritzky, A. R.; Patel, R. C.; Shanta, M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1888.

(40) Katritzky, A. R.; Liso, G.; Lunt, E.; Patel, R. C.; Thind, S. S.; Zia, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 849.

(41) Katritzky, A. R.; Lloyd, J. M.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 1* **1982**, 117.

(42) Kornblum, N.; Clutter, R. J.; Jones, W. J. *J. Am. Chem. Soc.* **1956**, *78*, 4003.

(43) "Dictionary of Organic Compounds" (under *p*-anisaldehyde).

2 h until TLC (silica, $CH_2Cl_2$) showed the reaction to be complete. The precipitated triphenylpyridine was filtered off, water (30 mL) added, and the whole extracted with ether (3 × 20 mL). The extract was washed with water (3 × 20 mL) and dried over anhydrous $MgSO_4$, and dry HCl was passed to remove residual triphenylpyridine, which was filtered off. The filtrate was evaporated and the crude product distilled (15 mmHg) to give 2-phenylnitroethane (yield 58%), bp 125–130 °C (15 mmHg) (lit.[2] bp 126 °C (14 mmHg)).

**Kinetic Procedure.** In a typical experiment, the pyridinium salt (0.08 mmol) was dissolved in 50 mL of $Me_2SO$. NaH (1.3 mmol) was weighed out and dissolved in 50 mL of 1-pentanol. 2-Nitropropane (1.3 mmol) was dissolved in 50 mL of $Me_2SO$ to give a third stock solution. All stock solutions were protected from light. Pentanolic sodium pentoxide (1 mL), 2-nitropropane in $Me_2SO$ (1 mL), and pyridinium salt in $Me_2SO$ (1 mL) were pipetted into $Me_2SO$ (ca. 20 mL) in a 25-mL measuring flask, and the volume was made up to the mark rapidly with more $Me_2SO$. The mixture was transferred to a 1-cm quartz UV cell and placed in a SP6-500 digital display spectrophotometer. The reaction rate was followed by measuring the decrease in absorption at the required wavelength at constant temperature. The infinity reading was recorded in each experiment after change in absorbance was negligible (ca. 2 h). Table A records a typical result (supplementary material section).

Reactions at 80–100 °C were conducted on aliquots (3 mL) of the UV-diluted reaction mixture placed in stoppered glass tubes in hot blocks. At fixed time intervals, the tubes were removed and cooled to 25 °C. The mixture was transferred to a 1-cm UV quartz cell and the absorbance noted.

**Acknowledgment.** We thank the Ministry of Education, Government of Pakistan, for a grant to Mr. M. A. Kashmiri.

**Registry No.** **1a**·$BF_4^-$, 66310-10-9; **1b**·$BF_4^-$, 71017-85-1; **1c**·$BF_4^-$, 72538-32-0; **1d**·$BF_4^-$, 71017-75-9; **1e**·$BF_4^-$, 83365-34-8; **1f**·$BF_4^-$, 2355-56-8; **1g**·$BF_4^-$, 66310-04-1; **1h**·$BF_4^-$, 73086-84-7; **1j**·$BF_4^-$, 81128-05-4; **2a**, 25854-38-0; **2b**, 25854-39-1; **2c**, 24163-39-1; **7**, 15519-25-2; **8**, 71670-94-5; **9**, 47484-87-7; **10**, 83365-35-9; **11**, 83365-36-0; **12**·$BF_4^-$, 75864-90-3; **13**, 75505-94-1; sodium nitrocyclohexanide, 4702-04-9; 2,4,4-trimethyl-2-nitropentane, 5342-78-9.

**Supplementary Material Available:** Tables of UV data, rate constants, and equilibrium constants (5 pages). Ordering information is given on any current masthead page.

---

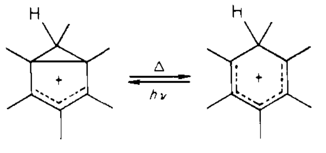
# Thermochemical Relationships between Some Bicyclohexenyl and Benzenium Cations[1]

**Ronald F. Childs* and D. Lindsay Mulholland**

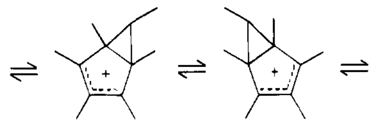
*Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada. Received May 26, 1982*

**Abstract:** The heats of protonation in $FSO_3H$ and solution in $CCl_4$ of penta- and hexamethylbenzene (**8** and **6**, respectively), hexamethyl(Dewar benzene) (**3**), 1,3,4,5,6-pentamethyl- and 1,3,4,5-tetramethyl-2-methylenebicyclo[3.1.0]hex-3-ene, (**7** and **9**, respectively), 2,3,4,4,5,6-hexamethyl-1-methylenecyclohexa-2,5-diene (**10**), 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one (**14**), and 1,3,4,5,6,6-hexamethylbicyclo[3.1.0]hex-3-en-2-one (**13**) were measured. The protonations were carried out at different temperatures such that different ions were formed. This enabled the relative heats of formation of the hexamethylbenzenium, **2**, hexamethylbicyclo[3.1.0]hexenyl, **1**, and hexamethylbicyclo[2.1.1]hexenyl cations, **4** and **5**, to be obtained. The magnitude of the energy differences is discussed in terms of the resonance energies of the cations. Similar thermochemical relationships were established for the hydroxy cations **15** and **16**.

The bicyclohexenyl cations are an important group of carbenium ions that are isomeric with the well-established benzenium ions. The bicyclo[3.1.0]hexenyl ions are related to the corresponding benzenium ions by a ground state forbidden, photochemically allowed, disrotatory electrocyclic reaction, eq 1.[2-5] While the thermally induced conversion of a bicyclo[3.1.0]hexenyl cation to a benzenium ion is a relatively difficult process, these bicyclic ions exhibit facile, highly stereoselective circumambulatory rearrangements, eq 2.



1 2 (1)



(2)

There are few reports of the preparation of stable bicyclo[2.1.1]hexenyl cations. The two hexamethyl-substituted ions shown in eq 3 have been prepared by protonation of hexamethyl(Dewar benzene).[6,7] These two ions rapidly interconvert at low temperatures, while at higher temperatures they undergo a slow, irreversible isomerization to the hexamethylbenzenium ion. The bicyclo[3.1.0]- and -[2.1.1]hexenyl cations are related to each other by 1,2 or 1,3 shifts of the bridging carbon, eq 4.

The photochemical and thermal interconversions of these ions have been studied extensively; however, there is a dearth of information on their thermochemistry, Sorensen and Rauk[8] have suggested the energy difference between the unsubstituted bicyclo[3.1.0]hexenyl and benzenium ions might be as high as 40 kcal/mol. Calculations at the 4-31G level indicate an energy difference of 34 kcal/mol.[9] No experimental information seems

---

[1] This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

[2] Childs, R. F.; Winstein, S. *J. Am. Chem. Soc.* **1974**, *96*, 6409; **1968**, *90*, 7146.

[3] Childs, R. F.; Sakai, M.; Parrington, B. D.; Winstein, S. *J. Am. Chem. Soc.* **1974**, *96*, 6403.

[4] Vogel, P.; Saunders, M.; Hasty, N. M., Jr.; Berson, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1551. Isaev, I. S.; Mamatyuk, V. I.; Kuzubova, L. I.; Gordymova, T. A.; Koptyug, V. A. *Zh. Org. Khim.* **1970**, *6*, 2482. Koptyug, V. A.; Kuzubova, L. I.; Isaev, I. S.; Mamatyuk, V. I. *Ibid.* **1970**, *6*, 2258.

[5] Koptyug, V. A.; Kuzubova, L. I.; Isaev, I. S.; Mamatyuk, V. I. *J. Chem. Soc. D.* **1969**, 389; *Zh. Org. Khim.* **1970**, *6*, 1843.

[6] Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas.* **1968**, *87*, 385, 1042; **1969**, *88*, 353.

[7] Paquette, L. A.; Krow, G. R.; Bollinger, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 7147.

[8] Sorensen, T. S.; Rauk, A. "Pericyclic Reactions"; Marchand, A. P.; Lehr, R. E., Eds.; Academic Press, New York, 1977; Vol. 2, p 1.

[9] Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 5207. Hehre, W. J.; Pople, J. A. *Ibid.* **1972**, *94*, 6901.