Tetrahedron Vol. 42, No. 1, pp. 101 to 108, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

THE NON-CHAIN RADICALOID C-ALKYLATION OF NITRONATE ANIONS: FURTHER EVIDENCE FOR THE MECHANISM

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(*Received in UK 24 September* 1985)

Abstract- The effects of the variation of solvent, pyridinium leaving group, N-substituent, and nitronate nucleophile have been studied in the C-alkylation of nitronate anions. These variations and studies of the effects of inhibitors, attempted entrainment reactions, and ESR work are all in accord with our previously suggested mechanism.

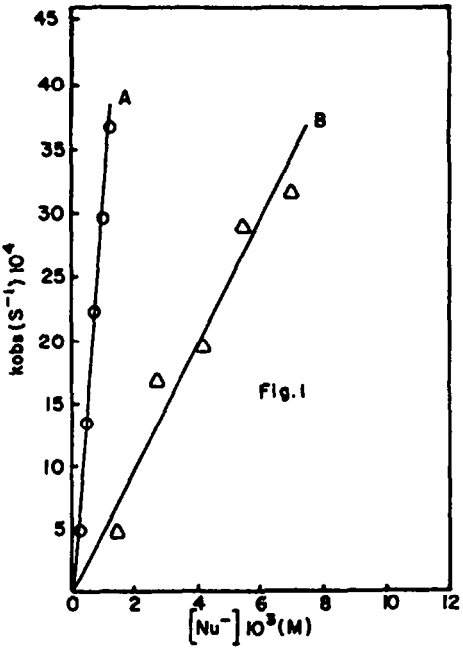
We claimed[1] recently that the C-alkylation of nitroalkane anions 2 by 1-alkyl-2,4,6-triphenylpyridinium cations 1[2] is a non-chain radicaloid nucleophilic substitution of a novel type (Scheme). In view of the considerable current interest in single electron transfer reactions,[3,4,5] and the fact that most known examples represent radical-chain rather than radical-cage processes,[6] we have further investigated our reaction. We now report kinetic work in which we have successively varied solvent, leaving group, N-substituent and nucleophile, and also studied the effects of inhibitors, attempted entrainment experiments, and carried out ESR and CIDNP work. We believe that these results provide strong confirmatory evidence for the mechanism proposed;[1] they have also enabled considerably milder and higher-yielding preparative conditions to be found.[7] However, the present work has also shown that the determination of the kinetics of reaction with nitroalkane anions in DMSO is difficult; unless the conditions are carefully defined (see Experimental) nonreproduceable results are obtained. We have therefore repeated virtually all the kinetic measurements reported[1]; some errors were uncovered, and are discussed later in the present paper, but the overall conclusions remain unaltered.

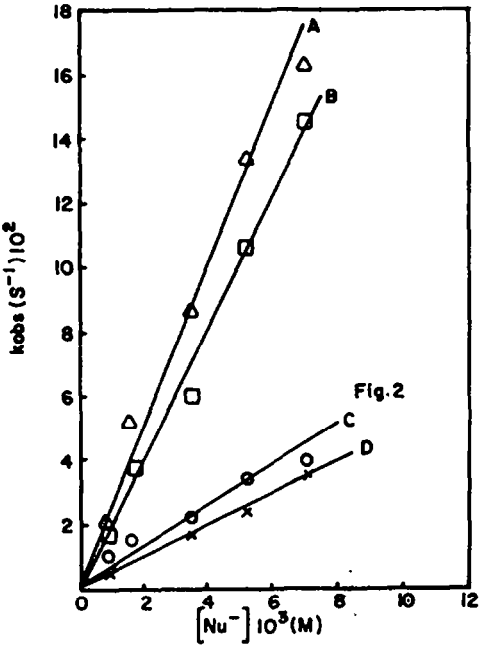
Effect of Solvent. Reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (1a) with excess sodium 2-nitropropanide (2a) (pseudo first-order conditions) in DMSO and sulfolane at various temperatures gave good straight line plots for $\ln(\text{epsilon}_1 - \text{epsilon}_\infty)/(\text{epsilon}_t - \text{epsilon}_\infty)$ vs. time, demonstrating first-order behavior for the substrate.[8] Plots of k_{obs} vs. $[Me_2CNO_2^-]$ are shown in Fig. 1, which demonstrates that these reactions are first order in nucleophile. The reaction is faster in DMSO than in sulfolane by a factor of ca. 30. Rates are much slower in n-pentanol and in diglyme (see Table 1).

The rates at 25 °C, and at higher temperatures, are recorded in Table 1: rough values for the activation parameters are calculated as E_a = 10.6 kcal mol^{-1} and activation entropy of -44 cal $mol^{-1}K^{-1}$ in DMSO, and E_a = 15.2 and activation entropy of -43 in sulfolane; we previously reported values in DMSO[2] of 4.3 and -58, respectively. The significance of the large negative activation entropies is not clear; for radical-cage reactions, positive values have been observed previously.[9]

Fig. 1. Dependence of k_{obs} on nucleophile concentration for the reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate with sodium 2-nitropropanide in (A) dimethyl sulfoxide at 25°C, (B) sulfolane at 45°C.

Fig. 2. Dependence of k_{obs} on nucleophile concentration for reactions with sodium 2-nitropropanide in DMSO at 25 °C of: (A) 1-benzyl-5,6-dihydro-2,4-diphenyl-1-azonia-11-thiabenzo[a]fluorene (11), (B) 1-benzyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[h]quinolinium (9a), (C) 1-benzyl-2-(2-thienyl)-4,6-diphenylpyridinium (7d), (D) 1-benzyl-2-t-butyl-4,6-diphenylpyridinium (7a) tetrafluoroborates.





We conclude that this reaction retains the same mechanism in sulfolane. Reaction mechanisms involving rate-determining CTC formation reported in the literature are rare, and solvent effects on free radical reactions, while measurable,[10] have been considered relatively unimportant.[11] The effect of solvent character on the present reaction rate is, however, not unreasonable: slower in protic solvents, and fastest in aprotic solvents of highest polarity.

Variation of Pyridinium Leaving Group. Reactions of the 1-benzylpyridinium cations (7a, 7d, 7e, 7j, 9a, and 11) with excess sodium 2-nitropropanide at 25 °C in DMSO all gave good straight line pseudo first-order plots.[8] Plots for k_{obs} vs. [nucleophile], shown in Fig. 2, indicate that the non-chain mechanism persists for these compounds.

TABLE 1. Rate constants for the reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate[a] with sodium 2-nitropropanide in different solvents

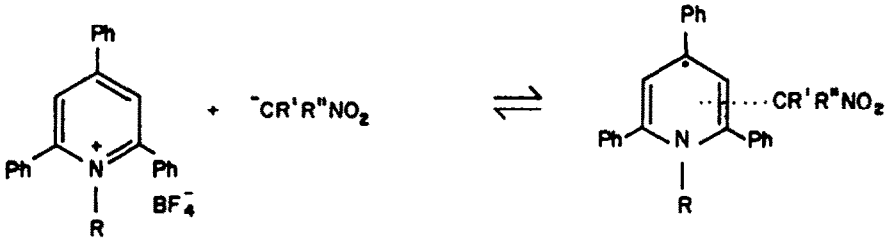
Temp. (°C)	Solvent	k_2[b] (l mol^{-1}s^{-1})	Temp. (°C)	Solvent	k_2[b] (l mol^{-1}s^{-1})
25	DMSO	4.88 ± 0.40	25	diglyme	<0.0002
35	DMSO	8.88 ± 0.65	45	sulfolane	0.46 ± 0.06
45	DMSO	14.76 ± 0.66	90	sulfolane	6.54 ± 0.06
25	n-pentanol	<0.0061			

Footnotes: a Concentration of pyridinium salt = 7.18 x10^{-5} mol l^{-1}. b Second-order rate constant obtained from the plot of k_{obs} (pseudo first-order rate constant) vs. [Nu$^-$] (90% confidence limits; intercepts not significantly different from zero).

TABLE 2. Second-order rate constants for the reactions of 1-benzylpyridinium tetrafluoroborates[a] with sodium 2-nitropropanide in DMSO at 25 °C.

No.	Pyridinium Cation Ring System	Substituent[b] C-2	C-6	k_2[c] (l mol^{-1}s^{-1})	Relative[d] Rate
1a	pyridine	Ph	Ph	4.88 ± 0.40	1.0
7a	pyridine	Bu^t	Ph	5.8 ± 0.3	1.2
7b	pyridine	$C_6H_4NO_2$-4	Ph	23.6 ± 1.0	4.8
7c	pyridine	C_6H_4OMe-4	Ph	5.5 ± 0.75	1.1
7d	pyridine	2-thienyl	Ph	6.3 ± 0.4	1.3
7e	pyridine	2-pyridyl	Ph	21.8 ± 1.9	4.5
7f	pyridine	$C_6H_3Me_2$-2,5	Ph	5.7 ± 0.4	1.2
7g	pyridine	$C_6H_3Cl_2$-2,5	Ph	6.5 ± 0.3	1.3
7h	pyridine	1-naphthyl	Ph	8.3 ± 0.9	1.7
7i	pyridine	2-naphthyl	Ph	11.3 ± 0.9	2.3
7j	pyridine	Pr^i	Ph	5.0 ± 0.55	1.0
8a	benzo[h]quinoline	Ph	Ph	23.0 ± 0.3[e]	4.7
9a	benzo[h]quinoline	Bu^t	-	18.3 ± 0.6	3.8
10	dibenz[c,h]acridine	-	-	128 ± 13[e]	26
11	benzothiopheno-[3,2-h]quinoline	Ph	-	24.7 ± 1.1	5.1

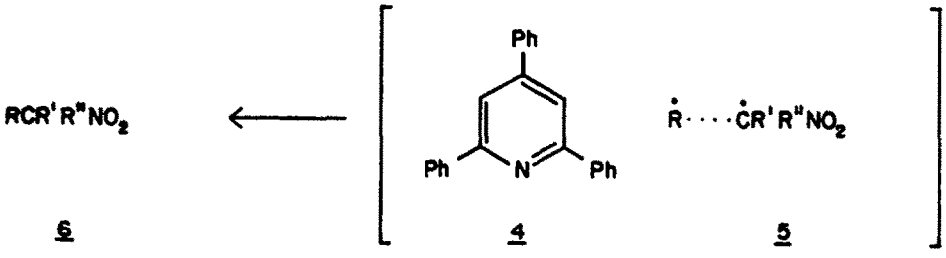
a Concentration range of pyridinium salt = 5.5-7.1 x 10^{-5} mol l^{-1}. b 4-Phenyl substituent in all cases. c Second-order rate constant obtained from plots of k_{obs} vs. [Nu$^-$] usually at 2 or 3 different substrate concentrations for each compound. d Relative to 1a. e Kinetic results given for these compounds in ref. 1 are incorrect; see text.



1 a; R = CH_2Ph
b; R = n-C_4H_9
c; R = $CH_2C_6H_4NO_2$-4

2 a; R' = R" = Me
b; R', R" = C_5H_{10}-cyclo
c; R' = H, R" = Me
d; R' = R" = H

3 a ; R' = R" = Me
b ; R', R" = C_5H_{10}-cyclo
c ; R' = H, R" = Me
d ; R' = R" = H



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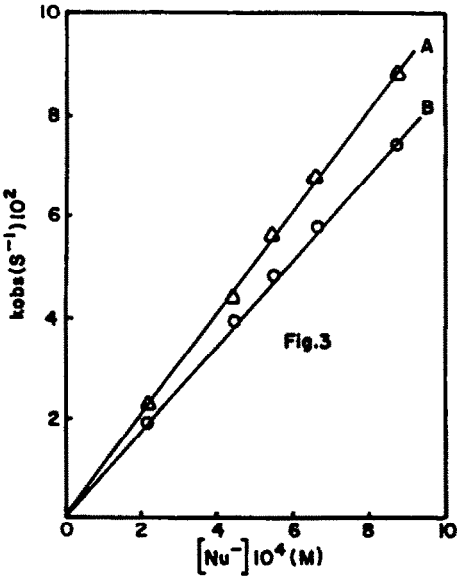
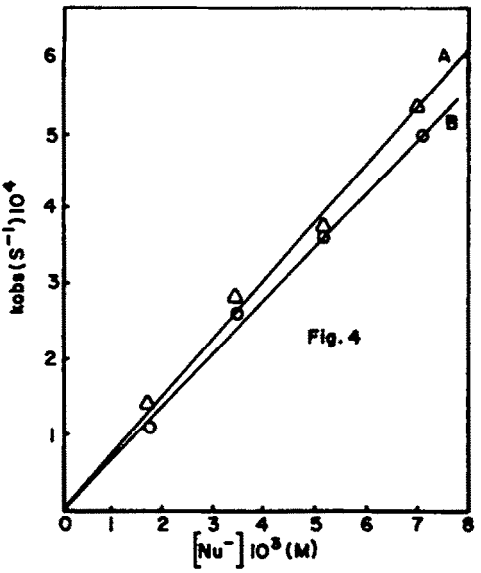
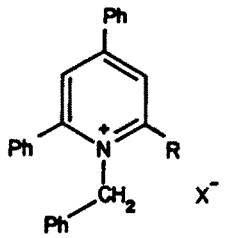
Scheme Non-chain radicaloid substitution mechanism

Fig. 3. Dependence of k_{obs} on nucleophile concentration for the reaction of 1-benzyl-5,6-dihydro-4-phenylbenzo[h]quinolinium (9a) in DMSO at 25 °C with (A) sodium nitromethanide, (B) sodium nitrocyclohexanide.

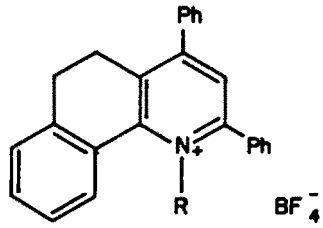
Fig. 4. Dependence of k_{obs} on nucleophile concentration for the reactions with sodium 2-nitropropanide at 25°C in DMSO of (A) 1-n-butyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[h]quinolinium (9b), (B) 1-n-butyl-2-t-butyl-4,6-diphenylpyridinium (12).



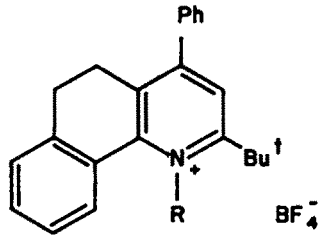




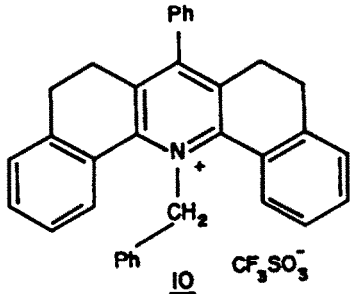
7 a; R = t-C_4H_9 X = CF_3SO_3
b; R = $C_6H_4NO_2$-4 X = CF_3SO_3
c; R = C_6H_4OMe-4 X = BF_4
d; R = 2-thienyl X = ClO_4
e; R = 2-pyridyl X = BF_4
f; R = $C_6H_3Me_2$-2,5 X = CF_3SO_3
g; R = $C_6H_3Cl_2$-2,5 X = CF_3SO_3
h; R = 1-naphthyl X = CF_3SO_3
i; R = 2-naphthyl X = CF_3SO_3
j; R = Pr^i X = BF_4



8 a; R = CH_2Ph
b; R = n-C_4H_9



9 a; R = CH_2Ph
b; R = n-C_4H_9



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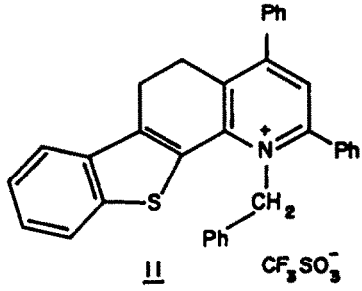

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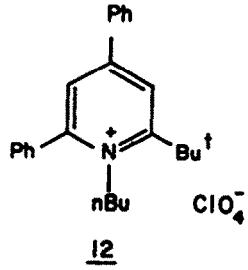

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TABLE 3. Second-order rate constants for reactions with nitroalkane anions in DMSO at 25 °C.

Nucleophile	1-Benzyl-2,4,6-triphenylpyridinium (1a) k_2 (l mol^{-1}s^{-1})	1-Benzyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[h]quinolinium (9a) k_2 (l mol^{-1}s^{-1})	Rate Ratio (k_{9a}/k_{1a})
$CMe_2NO_2^-$	7.74 ± 0.55	18.3 ± 0.6	3.8
$C(C_5H_{10})NO_2^-$	22.8 ± 0.3	86.8 ± 6.1	3.8
$CHMeNO_2^-$	3.65 ± 2.4	14.7 ± 0.7	4.0
$CH_2NO_2^-$	25.9 ± 0.8	103.7 ± 4.0	4.0

Second-order rate constants for the presently investigated compounds and other available results (Table 2) enable delineation of rate influences. The most striking thing about the rates given in Table 2 is that they vary only by a factor of 26, whereas for the S_N2 rates of compounds (1a), (8a) and (10) in piperidine a variation of 900 is found.[1] Rates are almost unchanged for the less conjugated 2-alkyl compounds (7a, 7j), for the 2-o-substituted aryl derivatives (7f, 7g), and for electron-donor substituted aryl pyridinium cations (7c). They are somewhat higher for electron-acceptor substituted phenyl derivatives (7b, 7e), for more conjugated monocyclic cations (7h, 7i), and for polycyclic compounds (8a, 9a and 11), especially for the most conjugated of all (10). [In our earlier report[1] we erroneously stated that the rates for cations (8a) and (10) were very much less than that for cation (1)].

Variation of Nitronate Nucleophile. We reported previously[1] that sodium nitrocyclohexanide (2b) shows kinetic results with 1-benzyl-2,4,6-triphenylpyridinium cation (1a) very similar to sodium 2-nitropropanide (2a), but with a larger k_2. Our present results (Table 3) indicate a factor of 2.9. For 1-benzyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[h]quinolium tetrafluoroborate (9a), results in Fig. 3 and Table 3 show that a rather similar factor (4.7) applies. The kinetic behavior of the reactions of both (1a) and (9a) with sodium nitroethanide (2c) are again similar (see Table 3); the rates are now somewhat smaller than those for nitropropanide, but the rate ratio (Table 3) is very comparable. Sodium nitromethanide reacts with cations (1a) and (9a) at about the same rate as the nitrocyclohexanide; again, the rate ratio k_{9a}/k_{1a} is similar.

TABLE 4. Second-order rate constants for the reactions of 1-n-butylpyridinium tetrafluoroborates[a] with sodium 2-nitropropanide in DMSO at 25°C

Pyridinium Salt	Ring System	2-Substituent	k_2 (l mol^{-1} s^{-1})
1b	pyridine	Ph	0.074 ± 0.004
12	pyridine	Bu^t	0.068 ± 0.002
8b	benzo[h]quinoline	Ph	0.080 ± 0.008
9b	benzo[h]quinoline	Bu^t	0.073 ± 0.008

a Concentration of pyridinium salt = 6.2-8.6 x 10^{-5} mol l^{-1}.

Variation of N-Substituent. N-n-Butyl analogues of some of the N-benzyl derivatives just considered were studied in a similar manner; again, good straight line plots (Fig. 4) indicate a similar mechanism. Rates for N-n-butyl compounds are shown in Table 4; here the rate variation is very small indeed, even less than is the case for the corresponding N-benzyl derivatives.

We reported previously[1] that sodium nitromethanide (2d) with 1-benzyl-2,4,6-triphenylpyridinium cation (1a) gave a CTC which then breaks down in a rate-determining first-order reaction at 25 °C to form the products; we now believe that these conclusions are qualitatively correct but that the presence of methoxide obscured the quantitative interpretation.

TABLE 5. Reaction of 1-benzylpyridinium salts and sodium 2-nitropropanide in DMSO at 25 °C in the presence of 1,4-dinitrobenzene.[a]

Pyridinium Salt	Ring System	Nucleophile conc. x 10^3 mol l^{-1}	Substrate conc.[a] x 10^5mol l^{-1}	k_2 $l\ mol^{-1}s^{-1}$	$k_2^{in.}$ $l\ mol^{-1}s^{-1}$	Inhibition %
1a	pyridine	0.88	5.75	4.88 ± 0.4	3.7 ± 0.3	25
7a	pyridine	3.49	7.31	5.8 ± 0.3	4.1 ± 0.3	29
7f	pyridine	3.49	6.07	5.7 ± 0.4	3.9 ± 0.2	31
9a	benzo[h]quinoline	3.49	7.10	18.3 ± 0.6	7.2 ± 0.7	60
10	dibenz[c,h]acridine	3.49	6.35	128 ± 13	39.1 ± 5.0	70

Footnote: a [Pyridinium Salt] = [Inhibitor]

Effect of Potential Inhibitors and Attempts at Entrainment. Table 5 records the results of kinetic runs carried out in the presence of an equal concentration of p-dinitrobenzene as a potential inhibitor. As seen from the Table, only ca. 30% inhibition was found for the monocyclic N-benzyl derivatives; the inhibition rose to 60-70% for the tri- and penta-cyclic pyridinium derivatives. In the case of cation (1a), five different concentrations of nucleophile were used and k_2 values obtained in the normal way; good linear plots for k_{obs} vs. [Nu^-] were found. At the inhibitor concentration used, very severe retardation has been reported for radical chain reactions.[12]

Radical chain reactions can sometimes be switched to an otherwise unreactive nucleophile by the technique of entrainment.[13] The reaction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (1a) with sodium azide in DMSO at 25 °C is immeasurably slow, both in the absence and the presence of catalytic amounts of sodium 2-nitropropanide. Thus, no entrainment takes place in our reaction, as expected for a non-chain mechanism.

Several pyridinium cations in solution in DMSO were mixed with sodium 2-nitropropanide and their ESR spectra measured at 77 K. Only broad unresolved spectra were found. No CIDNP effect was found.

Conclusions. At the time of our initial discovery[14] the only examples of the simple intermolecular C-alkylation of nitroalkane monoanions were a very limited range closely related to p-nitrobenzyl chloride.[15] Since then, C-alkylation has been reported for alkylmercury halides,[16] perfluoroalkyl iodides,[17] some chloromethylquinolines,[18] and certain alpha-haloketones[19] and C-arylation for diaryliodonium iodides.[20] All the alkylations are apparently chain processes, while the arylation is considered to go partly in a cage. The mechanism of $S_{RN}1$ radical chain processes is being increasingly investigated, steric effects defined and the complexity of the kinetics emphasized;[21] the present results will help define the significance of non-chain cage processes.

EXPERIMENTAL SECTION

Melting points were recorded on a Reichert hot stage microscope and are uncorrected. UV spectra of reactants and products (6.60×10^{-5} mol l^{-1}) were recorded on a Pye Unicam SP8-200 spectrophotometer. For the rate measurements, a Perkin Elmer 330 spectrophotometer (programmable) was used with a internal thermostat. ESR work was carried out using a Varian E-3 ESR spectrometer at a microwave power of 8.0 mW, a microwave frequency of 9.081-9.088 GHz, modulation amplitude of 1-10G and scan range of ±500G. All ^{1}H NMR spectra for the CIDNP experiments were recorded on a 100 MHz JEOL FX100 spectrometer equipped with a variable temperature probe.

Preparation of Compounds

1-Substituted-2,4,6-triphenylpyridinium tetrafluoroborates were made following literature methods from 2,4,6-triphenylpyrylium tetrafluoroborates[22] and the appropriate amine: 1-benzyl-(1a), mp 193-195 °C (lit.[23] mp 196-197 °C); 1-n-butyl-(1b), mp 201-203 °C (lit.[23] mp 201-202 °C); 1-(4-nitrobenzyl)-(1c), mp 132-133 °C (lit.[1] 133-134 °C).

1-Benzyl-2-substituted-4,6-diphenylpyridinium salts were prepared following literature methods from 2-substituted-4,6-diphenylpyrylium tetrafluoroborates[24-27] and benzylamine (vide supra for anion): 2-t-butyl-(7a), mp 193-194 °C (lit.[24] mp 193-195 °C); 4-nitrophenyl-(7b), mp 166-167 °C (lit.[28] mp 165-167 °C); 4-methoxyphenyl-(7c), mp 162-164 °C (Found: C, 70.8; H, 5.2; N, 2.8. $C_{31}H_{26}BF_4NO.\frac{1}{2}H_2O$ requires C, 71.0; H, 5.0; N, 2.7%); 2-(2-pyridyl)-(7e), mp 195-197 °C (lit.[19] mp 195-199 °C); 2,5-dimethylphenyl-(7f), mp 161-163 °C (lit.[28] mp 160-163°C); 2,5-dichlorophenyl-(7g), mp 94-96 °C (lit.[28] mp 95-96 °C); 1-naphthyl-(7h), mp 205-208 °C (lit.[28] mp 206-208 °C); 2-naphthyl-(7i), mp 109-112 °C (lit.[28] mp 109-111 °C); 2-isopropyl-(7j), mp 105-107 °C (lit.[27] mp 105-107 °C); 2-(2-thienyl)-(7d), mp 186-187 °C (lit.[26] mp 187 °C) was prepared as perchlorate salt.

1-Benzyl-5,6-dihydro-2,4-diphenylbenzo[h]quinolinium tetrafluoroborate (8a) was prepared by reacting 5,6-dihydro-2,4-diphenylbenzo[h]chromenylium tetrafluoroborate[24] with benzylamine: mp 192-194 °C (lit.[24] mp 193 °C). 1-n-Butyl-5,6-dihydro-2,4-diphenylbenzo[h]quinolinium tetrafluoroborate (8b) was prepared [24] by reacting 5,6-dihydro-2,4-diphenylbenzo[h]chromenylium tetrafluoroborate[24] with n-butylamine: mp 97-98 °C (lit.[24] mp 97-98 °C).

1-Substituted-2-t-butyl-5,6-dihydro-4-phenylbenzo[h]quinolinium tetrafluoroborates were prepared by reacting 2-t-butyl-5,6-dihydro-4-phenylbenzo[h]chromenylium tetrafluoroborate[29] with the appropriate amine: 1-benzyl-(9a), mp 149-151 °C (lit.[30] mp 145-147 °C); 1-n-butyl-(9b), mp 141-142 °C (lit.[30] mp 142-144 °C).

1-Benzyl-5,6,8,9-tetrahydro-7-phenyldibenz[c,h]acridinium perchlorate (10) was prepared[24] by reacting 5,6,8,9-tetrahydro-7-phenyldibenzo[c,h]xanthylium perchlorate with benzylamine: mp 278-280 °C (lit.[24] mp 279 °C).

1-Benzyl-5,6-dihydro-2,4-diphenyl-1-azonia-11-thiabenzo[a]fluorene trifluoromethanesulfonate (11) was prepared by a literature method,[31] mp 167-168 °C (lit.[31] mp 166-168 °C).

1-n-Butyl-2-t-butyl-4,6-diphenylpyridinium perchlorate (12) was prepared[24] by reacting 2-t-butyl-4,6-diphenylpyrylium perchlorate[29] with n-butylamine: mp 153-155 °C (lit.[24] mp 154-155 °C).

Kinetic Procedure

In a typical experiment, the pyridinium salt (0.08 mmol) was dissolved in 50 ml of DMSO. 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 DMSO to give a third stock solution. All stock solutions were flushed with N_2 and protected from light. Pentanolic sodium pentoxide (1 ml) and 2-nitropropane in DMSO (1 ml) were mixed, stood 30 min and the pyridinium salt in DMSO (1 ml) then added; the resulting solution was pipetted into DMSO (ca. 20 ml) in 25 ml volumetric flask, and the volume was made up to the mark rapidly with more DMSO. (For faster runs 10^{-4} M pyridinium salt was employed.) The mixture was transferred to a 1 cm quartz UV cell and the cell then placed in a Perkin Elmer 330 digital display spectrophotometer. The reaction rate was followed by measuring the decrease in absorbance at the required wavelength at constant temperature. The infinity reading was recorded in each experiment after change in absorbance was negligible (usually ca. 2h).

Reactions at 40-90 °C were conducted on aliquots (3 ml) of the reaction mixture diluted with DMSO (vide supra) and placed in stoppered glass tubes in hot blocks. At equal time-intervals, the tubes were removed and cooled to 25 °C. Each aliquot was transferred to a 1 cm UV quartz cell and the absorbance noted.

Pseudo first-order rate constants were calculated from the gradient of conventional plots of $\ln(\text{epsilon}_1-\text{epsilon}_\infty)/(\text{epsilon}_t-\text{epsilon}_\infty)$ vs. time. Such plots were linear to at least 85% completion. Second-order rate constants were determined from the plots of k_{obs} vs. nucleophile concentration.

Kinetic Experiments with Inhibitors

Several kinetic experiments were carried out using one equivalent (6.60×10^{-5} mol l^{-1}) of the radical inhibitors (p-dinitrobenzene and di-t-butylnitroxide) which have no significant absorptions at the kinetic wavelengths. Other experimental conditions were kept the same. All stock solutions were protected from light. Spectra of the UV 'infinite-time' reaction mixture corresponded well with that of the products.

CIDNP Work

In a typical experiment, 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (1a) (0.080 g, 0.16 mmol) and sodium 2-nitropropanide (0.11 g, 1.0 mmol) were dissolved in DMSO-d_6 (2 ml each), the solutions were mixed, and 0.5 ml of the reaction mixture transferred to an NMR tube. Spectra were recorded repeatedly at 25 °C over regular intervals (5 mins.). The probe temperature was then raised to 40, 80 and 100 °C, and spectra were recorded again, using freshly prepared solutions. A similar procedure was adopted for other pyridinium salts.

Entrainment Experiments

Some kinetic runs were carried out for the reaction of 1-benzyl-2-t-butyl-5,6-dihydro-4-phenylbenzo[h]quinolinium tetrafluoroborate (9a) (6.60×10^{-5} mol l^{-1}) with sodium azide ($0.66\text{-}2.64 \times 10^{-3}$ mol l^{-1}) in DMSO containing sodium 2-nitropropanide in catalytic amount (0.66×10^{-5} mol l^{-1}) as a reactive nucleophile. The second-order rate constant was extremely slow at 25 °C in the absence ($k_2 = 5.6 \pm 0.1 \times 10^{-3}$ l mol^{-1} s^{-1}) and the presence ($k_2 = 6.1 \pm 0.4 \times 10^{-3}$ l mol^{-1} s^{-1}) of sodium 2-nitropropanide[8] thereby showing an absence of any activation.

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