Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 12.[1] Regio- and Stereo-chemistry of Nucleophilic Displacement and Solvolysis Reactions of *N*-(α-Methylallyl)- and *N*-(α-Phenylethyl)-pyridiniums

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N-(α-Methylallyl)pyridiniums rearrange to the *N*-(γ-methylallyl) analogues in a process analogous to ion return. In the tricyclic series the process (9) ⟶ (4) occurs spontaneously. In the monocyclic series (1) can be isolated and thermally rearranged into (2); this rearrangement is intramolecular. *N*-(α-Phenylethyl)pyridiniums solvolyse in HOAc–NEt_3 with predominant inversion of configuration (90%). In the 2,4,6-triphenyl series this occurs spontaneously. The isolated 1-(α-phenylethyl)-2-isopropyl-4,6-diphenylpyridinium solvolyses in chlorobenzene with first-order kinetics and with racemisation.

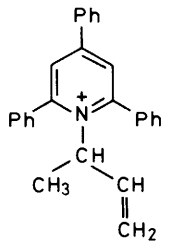
Previous studies[2] of the nucleophilic displacement of *N*-substituents for pyridinium rings have not included regio- and stereo-chemical studies at the reacting centre. We have now examined the possibility of S_N2' and S_N1' reactions in the displacement of allyl groups and the stereochemical consequences in the displacement of α-phenylethyl.

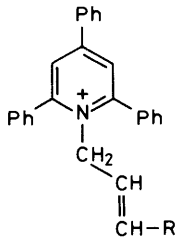
The S_N2' reaction of allyl compounds has been controversial[3] although several authentic cases have been claimed.[4] Bordwell has emphasized the importance of ion-pair intermediates in such reactions,[5] but McLennan has implicitly defended the traditional mechanistic picture,[6] and evidence has been presented for it.[7] The stereochemistry of the S_N2' transition state has been investigated theoretically.[8]

Several previous studies have been made of the stereochemical course of nucleophilic rearrangements involving the α-phenylethyl group. Solvolyses of 1-phenylethyl halides commonly yield net inversion (see ref. 9). Recently, Müller and Thi[10] found that the ditosylimide PhCHMe–NTs_2 reacted with PhS^- with inversion (no detectable racemization). By contrast Okamoto[11–14] and his co-workers have found that, in phenolic solvents, 1-phenylethyl derivatives solvolyse with retention accompanied by racemisation; this has been explained by an S_Ni four-centre mechanism.[11] The products from phenol[13] or 2,6-disubstituted phenols[12] as solvent are predominantly ethers with predominant retention, together with some *C*-alkylation with predominant inversion.[14]

Reactions of α- and γ-Methylallylamine with Pyryliums.— 2,4,6-Triphenylpyrylium gave the expected pyridinium salts (1) and (2), respectively (Table 1). These salts had very similar i.r. spectra, but were readily distinguished by their ^1H and especially ^{13}C n.m.r. spectra (Table 2). The ^{13}C n.m.r. spectra showed the expected sp^3 hybridized carbon signals: quartets for the CH_3 groups in both (1) and (2) with also a doublet in (1) for CH, and a triplet in (2) for the CH_2 group signal.

The reaction of 5,6-dihydro-2,4-diphenylbenzo[*h*]chromenylium (6) with γ-methylallylamine gave the expected salt (4) (Table 1) identified especially by its ^{13}C n.m.r. spectra (Table 2). This showed the CH_3 as a quartet at δ 17.6 and the CH_2 as a triplet at 60.6 p.p.m.: these chemical shifts are close to those found for the corresponding compound (2) (Table 2). The reaction of 5,6-dihydro-2,4-diphenylbenzo[*h*]-chromenylium (6) with α-methylallylamine also gave (4), identical to that obtained from (6) and γ-methylallylamine. We believe that the α-methyl salt (9) was formed initially, but


(1)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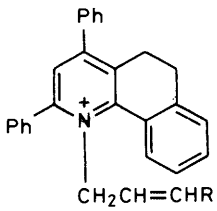
(3) R = H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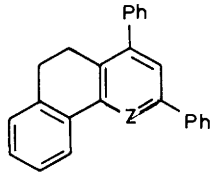
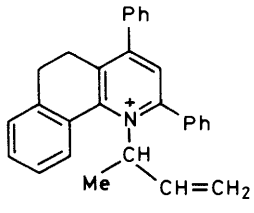
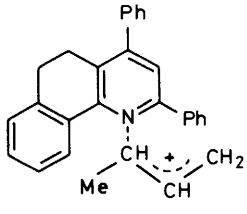

(6) Z = O^+
(7) Z = N
(8) Z = N^+R


(9)


(10)

is unstable and changes spontaneously into the γ-isomer (4). We have shown previously that the tricyclic pyridine (7) is a much better leaving group than its triphenyl analogue (12) and we believe that the spontaneous change (9) ⟶ (4) involves an ion–molecule intermediate (10) which collapses to (4) by

Table 1. Preparation of pyridinium tetrafluoroborates

Compd.	Time (h) before addition of Me-COOH	Time (h) after addition of Me-COOH	Crystallisation solvent	Crystal form	M.p. (°C)	Yield (%)
(1)	1	5	95% EtOH	Microprisms	123—125 (dec.)	83
(2)	1	5	96% EtOH	Prisms	94—96	80
(4)	1	5	CH_2Cl_2–Et_2O	Microprisms	95—100 (dec.)	80

Compd.	Found (%) C	Found (%) H	Found (%) N	Molecular formula	Required (%) C	Required (%) H	Required (%) N
(1)	72.1	5.4	3.1	$C_{27}H_{24}BF_4N$	72.2	5.4	3.1
(2)	72.2	5.4	3.1	$C_{27}H_{24}BF_4N$	72.2	5.4	3.1
(4)	73.1	5.6	2.9	$C_{29}H_{26}BF_4N$	73.3	5.5	2.9

Table 2. ^1H and ^{13}C n.m.r. chemical shift (p.p.m.) for pyridinium salts (1), (2), and (4)

	^1H N.m.r.[a]						^{13}C N.m.r.[a]			
	CH_3 (3 H, d)		Other allyl (4 H, m)	Aryl (m)		Ethylene bridge (4 H, s)	Before heating		After heating	
Compd.	δ	*J*/Hz	δ	δ	H	δ	CH_3	α-CH or CH_2	CH_3	α-CH or CH_2
(1)	1.47	7	4.50—6.25	7.15—7.95	17		19.7 [c]	65.7 [d]	17.3 [b,c]	56.9 [b,e]
(2)	1.45	7	4.83—5.15	7.35—7.95	17		17.5 [c]	56.9 [e]	17.5 [c]	56.9 [e]
(4)	1.40	5	4.90—5.63	7.20—8.20	15	2.88	17.6 [c]	60.6 [e]		

[a] $CDCl_3$ as solvent and $SiMe_4$ as internal standard. [b] $CDCl_3$ + CF_3CO_2H as solvent. [c] Quartet. [d] Doublet. [e] Triplet. Footnotes *c*—*e* apply to the off resonance spectra.

a process analogous to ion return. This explanation is supported by the behaviour in the analogous monocyclic series.

Conversion of 1-(α-*Methylallyl*)- *into* 1-(γ-*Methylallyl*)-2,4,6-*triphenylpyridinium*.—The α-methyl compound (1) melts at 123—125 °C, but on cooling until solidification and reheating, it melts again at 80—90 °C [*cf.*, γ-isomer (2), m.p. 94—96 °C]. The ^1H and ^{13}C n.m.r. spectra of the γ-isomer (2) do not change after the compound has been kept at 130 °C in the molten state for 20 min. After 20 min in the molten state at 130 °C, the α-isomer (1) shows ^1H and ^{13}C n.m.r. spectra which are changed and are now very similar to those for (2).

Heating the 10% solution of α-methyl compound (1) in chlorobenzene–CF_3CO_2H at 100 °C, after *ca.* 10 min the ^1H n.m.r. spectrum begins to change; after *ca.* 1 h, the spectrum becomes qualitatively similar to that for γ-methyl compound (2). On treating compound (2) in the same way, the ^1H n.m.r. spectrum remains unchanged over 24 h. The α-isomer (1) was changed to the γ-methyl compound (2) under preparative conditions by heating for 1 h at 100 °C. This interconversion is clearly intramolecular considering the low tendency for (1) to undergo S_N2 displacement (see later).

This intramolecular conversion must involve the methylallyl carbonium ion solvated by triphenylpyridine, an ion–molecule pair which undergoes collapse to the new product. This process is analogous to ion-pair return.

Kinetics of Reaction of N-*Allylpyridiniums* (1)—(3) *with Piperidine*.—Following earlier work in this series,[15] reactions were carried out in chlorobenzene solution. For (2) and (4) plots of k_{obs} obtained under pseudo-first-order conditions (Table 3) against [piperidine] gave straight lines which passed through the origin: the absence of significant intercepts shows the absence of S_N1, *i.e.* pure S_N2 behaviour (Table 4). Compared to the corresponding allyl compounds at 100 °C [(3) and (5)] [16] the k_2 value is three times higher for both the monocyclic derivative (2) and the tricyclic analogue (4) [for compound (4) the rate at 100 °C was estimated assuming an average $\Delta H^{\ddagger}_{373}$ of 16 kcal mol^{-1}, as observed for the analogous reactions of other *N*-substituted tricyclics (8); *cf.* refs. 16 and 17]. This finding is in agreement with the rate increase found for γ-methyl substitution in the reaction of γ-methylallyl chloride with ethoxide ion in ethanol and with iodide in acetone.[18]

By contrast with what was observed for (2) and (4) the α-methylallyl compound (1) showed a large S_N1 component (Table 4). Because of this, k_2 for the S_N2 component for (1) is subject to a large error although it is almost certainly larger than the k_2 for (2). This is in contrast to the effect of α-methyl substitution in the reactions of α-methylallyl chloride with ethoxide ion in ethanol and with lithium chloride in acetone, which decrease rates 20 and 36 times respectively.[18] The relative k_2 for (1) and (2) recalls the higher relative S_N2 rates found for secondary alkyl groups as compared to primary alkyl for these compounds with pyridinium leaving groups.[16]

The S_N1 component for (1) shows a k_1 value which is *ca.* 18 times * that found [16] for the *N*-s-butyl analogue (14).

* Ratio at 80 °C; k_1 value for the *N*-s-butyl analogue at 80 °C was estimated as 0.41 assuming an average $\Delta H^{\ddagger}_{373}$ of 28 kcal mol^{-1}, as observed for the S_N1 reactions of monocyclic compound (13) and tricyclic compound (8) (see refs. 16 and 19).

Table 3. Pseudo-first-order rate constants (k_{obs}) for the reactions of pyridiniums (1), (2), (4), and (17)—(19) with piperidine in chlorobenzene

Pyridinium (t/°C)	[Piperidine]/mol l^{-1}	$10^5 k_{obs}/s^{-1}$	Pyridinium (t/°C)	[Piperidine]/mol l^{-1}	$10^5 k_{obs}/s^{-1}$
(1) [a,b]	0.000 80	64	(17) [c]	0.001 60	179
(80)	0.001 20	64	(80)	0.002 40	176
	0.001 60	61		0.003 20	186
	0.002 40	77		0.004 80	177
	0.003 20	75		0.006 40	145
(2) [a]	0.0800	27.7	(18) [c]	0.0640	3.1
(100)	0.160	52.5	(60)	0.0960	3.7
	0.320	99.3		0.160	6.6
(4) [c,d]	0.009 60	11.6		0.192	7.0
(60)	0.0192	23.1	(18) [c]	0.001 60	25.4
	0.0320	35.8	(80)	0.003 20	25.5
	0.0640	67.7		0.004 80	26.0
(4) [c]	0.0320	18.2	(18) [c]	0.001 60	171
(50)	0.0480	26.4	(100)	0.003 20	157
	0.0640	34.8		0.004 80	160
(17) [c]	0.008 00	16.9		0.008 00	165
(60)	0.006 40	17.0	(19) [b,c]	0.001 60	4.6
	0.009 60	16.9	(100)	0.003 20	5.0
				0.006 40	6.5
				0.009 60	7.8

[a] Concentration of substrate 3.2×10^{-5} mol l^{-1}. [b] Kinetics followed up to 60% conversion, above which curvature of the plots of $\ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time was observed. [c] Concentration of substrate 6.40×10^{-5} mol l^{-1}. [d] Perchlorate.

Table 4. First- and second-order rate constants (k_1 and k_2) for the reactions of pyridiniums with piperidine in chlorobenzene

Pyridinium	t/°C	N [a]	b	$10^3 k_2$ [c,d]/l mol^{-1} s^{-1}	% Error	$10^5 k_1$ [c,d]/s^{-1}	% Error	$\frac{10^3 k_1}{k_2 + 10k_1}$ [e]
(1)	80	5	0.821	(62 ± 58)		57 ± 12	21	>5
(2)	100	3	0.9999	2.98 ± 0.27	9	(4.3 ± 5.8)		<25
(4)	50	3	0.9999	5.19 ± 0.23	4	(1.6 ± 1.1)		<5
	60	4	0.9997	11.1 ± 0.6	5	(1.2 ± 2.0)		<3
(17)	60	3	0.2846	(0.02 ± 0.51)		17.0 ± 0.3	2	>76
	80	5	−0.7683	(−63 ± 72)		196 ± 29	20	>69
(18)	60	4	0.984	0.33 ± 0.13	38	(0.8 ± 1.7)		<43
	80	3	0.933	(1.9 ± 4.5)		25.0 ± 1.6	6	>28
	100	3	−0.1831	(−4.1 ± 46)		165 ± 23	14	>28
(19)	100	4	0.997	4.09 ± 0.63	15	3.87 ± 0.38	10	9

[a] Number of runs. [b] Correlation coefficient. [c] 90% Confidence limit. [d] Values in parentheses not significantly different from zero. [e] Percent of reaction by S_N1 route at [piperidine] 10^{-1} mol l^{-1}.

Inversion of the Configuration of D-(+)-α-*Methylbenzylamine*.—We have shown previously [20] that reaction of 2,4,6-triphenylpyrylium salts (11) with α-phenylethylamine results in the spontaneous formation of solvolysis products: if triethylamine–acetic acid is used as solvent the product is the acetate (16), formed *via* (15).

When D-(+)-α-methylbenzylamine was reacted with 2,4,6-triphenylpyrylium tetrafluoroborate in triethylamine–acetic acid solution, the dextrorotatory amine was converted to the levorotatory acetate (16) on reaction at 24 °C for 48 h. The specific rotation of the 1-(−)-α-methylbenzyl acetate (16) indicates that the reaction proceeded with *ca.* 90% inversion It is proposed that the reaction takes place *via* the S_N2 mechanism (*cf.* the recent result with the ditosylimide).[10]

Kinetic Investigation of 1-(α-*Methylbenzyl*)*pyridiniums*.—It is possible to isolate such pyridiniums when the corresponding pyridine is a poorer leaving group than the 2,4,6-triphenyl derivative. We have investigated kinetically the mono- (17) and di-isopropyl compounds (18) and the fused ring derivative (19).[21] Kinetic results for these compounds are included in Tables 3—5 [(19) gave curved plots above 60% conversion, probably due to α-deprotonation, *cf.* ref. 22].

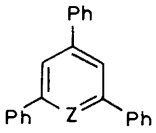
The reaction of the di-isopropyl derivative (18) with piperidine takes place predominantly by the S_N2 route at 60 °C, but mainly by S_N1 at 80 and 100 °C: the temperature coefficients for S_N1 reactions are known to be larger than those for S_N2. From the data of Table 4, for (18) by S_N1 reaction a rough $\Delta H^{\ddagger}$ of 24 kcal mol^{-1} can be calculated. These values can be compared with the average value of $\Delta H^{\ddagger}$ 28 kcal mol^{-1} found previously for the S_N1 reactions of *N*-s-alkylpyridiniums.[16,19]

The mono-isopropyl compound (17) reacts very predominantly by the S_N1 rate at both 60 and 80 °C. A rough value of $\Delta H^{\ddagger}$ for (17) was calculated as 28 kcal mol^{-1}.

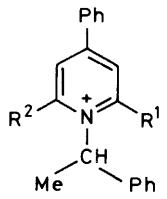
Relative Rates of 1-(α-*Methylbenzyl*)*pyridiniums*.—The S_N1 rates of (17)—(19) were extrapolated to 100 °C for comparison with the S_N1 rate of 1-s-butyl-2,4,6-triphenylpyridinium (14).[16] All the 1-(α-methylbenzyl) derivatives show faster S_N1 rates, but the factors vary considerably: 540, 50, and 1.2 for (17)—(19), respectively. As expected (17) is faster than (18); the rather slow rate for (19) underlines the small steric influence of the five-membered fused ring.

The S_N2 rate of (19) is at 100 °C *ca.* 20 times as fast as that [16] for the *N*-benzyl analogue (20).

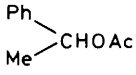
Stereochemistry of Reaction of 1-(α-*Methylbenzyl*)-2-*isopropyl*-4,6-*diphenylpyridinium* (17).—Reaction of (17) with diethylamine, piperidine, or dibenzylamine in chlorobenzene



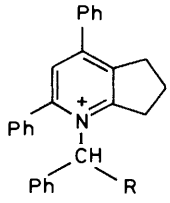
(11) Z = O^+
(12) Z = N
(13) Z = $N^+CHR^1R^2$
(14) Z = N^+s-C_4H_9



(15) $R^1 = R^2$ = Ph
(17) R^1 = Ph, R^2 = Pr^i
(18) $R^1 = R^2 = Pr^i$



(16)



(19) R = Me
(20) R = H

at 80 °C led to complete loss of optical activity. However, reaction of (17) with triethylamine–acetic acid gave the acetate of inverted configuration in accord with the results reported above for the reaction of α-phenylethylamine with triphenylpyrylium under these conditions.

Experimental

M.p.s and b.p.s are uncorrected. M.p.s were determined with a Kofler hot-stage apparatus. Spectra were measured with the following instruments: i.r., Perkin-Elmer 283B; ^{1}H n.m.r., Varian A-60A or EM-360L; ^{13}C n.m.r., JEOL JNM-FX-100 (25.0) operating in the Fourier transform mode; u.v.–visible, Unicam SP8-200. The optical rotations were taken with a Perkin-Elmer model 141 polarimeter using a cell with path-length 1 dm.

Elemental analyses were performed by Atlantic Microlab, Inc.

The preparation of the following compounds has been reported: [21] 1-(α-methylbenzyl)-2-isopropyl-4,6-diphenylpyridinium (17), m.p. 229—231 °C; 1-(α-methylbenzyl)-2,6-di-isopropyl-4-phenylpyridinium (18), m.p. 133—135 °C; 1-(α-methylbenzyl)-4,6-diphenyl-5*H*-cyclopenta[*b*]pyridinium (19), m.p. 150—152 °C, all as the tetrafluoroborate.

General Method for Preparation of Pyridiniums.—The appropriate amine (0.005 mol) and triethylamine (0.005 mol) were added to the pyrylium tetrafluoroborate (0.005 mol) suspended in dichloromethane (15 ml). The resulting solution was stirred at 24 °C for 1 h. Acetic acid (0.005 mol) was added and the mixture stirred for further 5 h. Dilution with ether (125 ml) gave the pyridinium. Each of the products was identified by m.p., t.l.c., i.r., u.v., ^{1}H n.m.r., and ^{13}C n.m.r. spectra, and elemental analysis. Details of reaction conditions and spectral data are collected in Tables 1 and 2, respectively.

Isomerization of 1-α-*Methylallyl*-2,4,6-*triphenylpyridinium.* (1).—A small sample tube containing pyridinium (0.1 g) was placed in an oil-bath at 130 °C for 20 min. After the pyridinium was melted, it was stirred occasionally. The product of isomerization was cooled and dissolved in $CDCl_3$ (0.5 ml) (if necessary, a few drops of CF_3CO_2H were added into $CDCl_3$ solution) and then the ^{1}H and ^{13}C n.m.r. spectra of the solution were taken.

(2). Pyridinium (0.05 g) was dissolved in chlorobenzene (0.5 ml) (if necessary, two or three drops of CF_3CO_2H were added). The resulting solution was transferred into a n.m.r. tube and then the tube was kept in a hot block at 100 °C for some time required. The ^{1}H n.m.r. spectrum was measured at different time intervals until the spectrum remained unchanged. The stability of 1-γ-methylallyl-2,4,6-triphenylpyridinium was measured in the same manner.

Table 5. Extinction coefficients for pyridinium cations and the corresponding pyridines at kinetic wavelength

Pyridinium	Kinetic wavelength λ/nm	ε_1 (for pyridinium)	ε_2 (for pyridine)
(1)	304	33 000 [a]	7 600 [a]
(2)	304	33 000 [a]	7 600 [a]
(4)	346	16 000 [b]	1 000 [b]
(17)	298	26 500 [b]	7 600 [b]
(18)	290	24 000 [b]	400 [b]
(19)	298	25 000 [b]	9 000 [b]

[a] In 2% (v/v) PhCl–EtOH. [b] In PhCl.

Isolation of Product of Isomerisation of 1-α-*Methylallyl*-2,4,6-*triphenylpyridinium.*—The pyridinium (0.5 g) in chlorobenzene (5 ml) was heated at 100 °C for 1 h. Ether (40 ml) was added to the cold mixture. The resulting solid in dichloromethane (2 ml) was treated with ether (30 ml) to give the isomer (0.22 g, 44%) which crystallised from CH_2Cl_2–Et_2O, m.p. 93—96 °C, and i.r. and ^{1}H n.m.r. spectra identical to those of 1-(γ-methylallyl)-2,4,6-triphenylpyridinium tetrafluoroborate.

Kinetic Measurements.—The kinetics were followed by u.v. spectrophotometry using the procedure already described.[15] In typical runs under pseudo-first-order conditions, the concentration of pyridinium was either 1.6×10^{-3} or 3.2×10^{-5} mol l^{-1}, while those of piperidine ranged from 0.0096 to 0.32 mol l^{-1}. Pseudo-first-order rate constants were calculated as the slope of the plot of $\ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time. For definition and calculation of errors, and for estimation of the precision of k_{obs}, see ref. 23. First- and second-order rate constants were obtained respectively as the intercept and the slope of the plot of k_{obs} *versus* [piperidine].

The kinetic results are listed in Tables 3 and 4. Extinction coefficients of the pyridiniums and corresponding pyridines at the kinetic wavelength are reported in Table 5.

Preparation of α-*Methylbenzyl Acetate.*—2,4,6-Triphenylpyrylium tetrafluoroborate (2.0 g, 5 mmol) was added to a stirred mixture of triethylamine (20.2 g, 0.2 mol), acetic acid (18 g, 0.3 mol), and D-(+)-α-methylbenzylamine (0.88 g, 7.4 mmol). The solution was stirred at 24 °C for 48 h, diluted with water (100 ml), extracted with ether (3 × 50 ml), washed with water (2 × 40 ml), and dried ($MgSO_4$). Dry HCl gas was passed and the pyridine hydrochloride filtered off. Evaporation down gave an orange oil which was distilled to give the acetate (16) (0.52 g, 63.4%) as a yellow oil, b.p. 48 °C at 0.5 mmHg (lit.,[24] 210—212 °C at 760 mmHg); δ 1.54 (3 H, d, *J* 7 Hz), 2.05 (3 H, s), 5.93 (1 H, q, *J* 7 Hz), and 7.35 (5 H, s); specific rotation $[\alpha]^{24}_{589}$ −98.3° (in EtOH) [lit.,[25] $[\alpha]^{D}_{28}$ −112.9° (in benzene)].

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