Reductive Deamination of Primary Amines [1,2]

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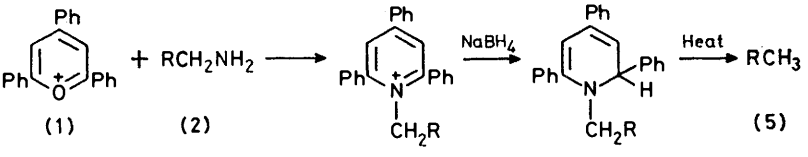
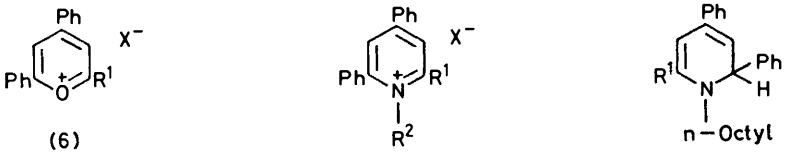
1-Alkyl-1,2-dihydropyridines thermolyse to complex mixtures, but 1-alkyl-2,3,5,6-tetraphenyl-1,4-dihydropyridines (prepared from the amine and 2,3,5,6-tetraphenylpyrylium salts followed by $NaBH_4$) give alkanes smoothly at *ca.* 200 °C.

Thermolysis of 1-benzyl-2-deuterio-2,4,6-triphenyl-1,2-dihydropyridine gives ω-monodeuteriotoluene (as shown by ^2H n.m.r. spectroscopy) indicating a radical mechanism.

We have shown that primary amines with βγ-unsaturation (*e.g.* allylamine, benzylamine) may be reductively deaminated utilising 2,4,6-triphenylpyrylium (1) in the three-stage sequence: amine (2) ⟶ pyridinium cation (3) ⟶ 1,2-dihydropyridine (4) ⟶ hydrocarbon (5).[3] We now describe attempts, eventually successful, to find a similar sequence that would be of general utility for the reductive deamination of alkyl amines (without βγ-unsaturation) and also the elucidation of the mechanism of conversion of benzylamine into toluene earlier described.[3]



(1) (2) (3) (4) (5)



(6) (7) (8)

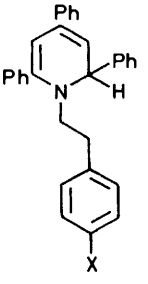
a; R^1 = Ph, X = BF_4

b; R^1 = Bu^t, X = ClO_4

	X	R^1	R^2
a	ClO_4	Bu^t	n-C_8H_{17}
b	ClO_4	Ph	n-C_8H_{17}
c	BF_4	Ph	n-C_8H_{17}
d	BF_4	Ph	$PhCH_2CH_2$
e	BF_4	Ph	$ClC_6H_4CH_2CH_2$(*p*)
f	BF_4	Ph	$PhCH_2$

(8) a; R^1 = Ph; b; R^1 = Bu^t

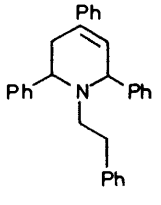
Reduction and Subsequent Pyrolysis of 2,4,6-Trisubstituted Pyridinium Salts.—2,4,6-Triphenylpyrylium tetrafluoroborate (6a) and 2-t-butyl-4,6-diphenylpyrylium perchlorate (6b) [4] reacted with primary amines to give pyridinium salts (see Table 1) characterised by microanalysis and spectral data. The *N*-octyl salts (7a) and (7c) reacted with sodium borohydride to give the 1,2-dihydropyridines (8b) and (8a) respectively as unstable oils which darkened spontaneously on standing and completely decomposed within 24 h at 25 °C. Both compounds (8a) and (8b) were characterised by their ^1H n.m.r. spectra (Table 2): 2-H at δ 3.5 was coupled with 3-H which also showed as a doublet at a lower field, 5-H resonated as a singlet at δ 5.6, and the chemically nonequivalent N-CH_2 protons appeared at δ 3.1 and 2.6.



(9)

a; X = H

b; X = Cl



(10)

Reduction of the 1-(2-phenylethyl)pyridinium salt (7d) under the same conditions as for the reduction of

TABLE 1

Preparation of 2,4,6-triphenyl- and 2-t-butyl-4,6-diphenylpyridinium salts (7)

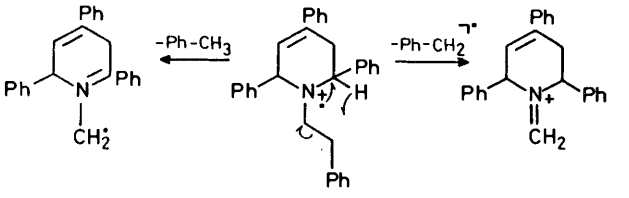
Comp. no.	R^1	R^2	Anion	Conditions for preparation: Solvent	Time (h)	Temp (°C)	Recryst. solvent	Yield (%)	Crystal form [a]	M.p. (°C)	Found (%): C	H	N	Formula	Required (%): C	H	N
(7a)	But	n-C_8H_{17}	ClO_4	Abs. EtOH	2	Reflux	EtOH–Et_2O	38	P	146—147	69.8	7.5	2.9	$C_{29}H_{36}ClNO_4$	69.7	7.7	2.8
(7b)	Ph	n-C_8H_{17}	ClO_4	EtOH	*b*		EtOH	*b*	N	160—161	71.8	6.6	2.6	$C_{31}H_{34}ClNO_4$	71.6	6.6	2.7
(7c)	Ph	n-C_8H_{17}	BF_4	Abs. EtOH	12	25	Abs. EtOH	39	N	149—150 *c*							
(7d)	Ph	$PhCH_2CH_2$	BF_4	Abs. EtOH	12	25	EtOH	85	P	273 *d*							
(7e)	Ph	$ClC_6H_4CH_2CH_2$(*p*)	BF_4	Abs. EtOH	12	25	EtOH	66	P	152—153	69.6	5.0	2.9	$C_{31}H_{25}BClF_4N$	69.8	4.7	2.6
(7f)	Ph	$PhCH_2$	BF_4	EtOH	12	20	Abs. EtOH	66	N	190—192 *e*							

[a] M denotes microcrystals; P, prisms; and N, needles. [b] Salt (7b) was obtained from salt (7c) by ion exchange. [c] Lit. m.p. 155 °C. [d] Lit.[21b] m.p. 274. [e] Lit.,[21] m.p 196—197.

salts (7a) and (7c), gave the 1,2,3,6-tetrahydropyridine (10). The expected 1,2-dihydropyridine derivative (9a) evidently undergoes further reduction by the mechanism initially postulated by one of us [5] and later proved experimentally by Anderson and Lyle *et al.*[6] The structural assignment of compound (10) follows from n.m.r. spectra: the proton decoupled ^{13}C spectrum (Table 2) shows 19 lines indicating effective equivalence of the 2- and 6-phenyl ring carbon atoms; the off-resonance spectrum of the non-aromatic peaks is especially characteristic. Double-resonance experiments allowed assignment of the ^1H n.m.r. spectrum as in Table 2. The mass spectrum showed the parent peak *m/e* 415 (8%) and the base peak at *m/e* 323 (loss of $PhCH_3$) but no peak corresponding to (M — 105) (loss of $PhCH_2CH_2$): the initial fragmentation of Scheme 1 is suggested.

The β-(*p*-chlorophenyl)ethyl derivative (7e) was reduced by sodium borohydride to the 1,2-dihydropyridine (9b) (68%), an unstable yellow oil, characterised by the ^1H n.m.r. pattern (see Table 2). The dihydropyridine (9b) precipitates out of the reaction mixture whilst (9a) being more soluble remains in solution and this probably explains its further reduction to the tetrahydropyridine (10).

Thermolysis of the above dihydropyridines under conditions similar to those used for the corresponding 1-(βγ-unsaturated)-1,2-dihydro-2,4,6-triphenylpyridines [3] yielded in all cases complex mixtures as shown by t.l.c.[7] That the reaction takes place even when the substituent quaternising the nitrogen is fully saturated, suggests a radical process. This radical reaction path is supported by the thermolysis of the tetrahydropyridine (10) which gave toluene in 53% yield, a result foreshadowed by the mass spectrum with its base peak at



SCHEME 1

(M — 92). Bond dissociation energies [8] show that it is easier to produce a benzyl radical from ethylbenzene $D(PhCH_2–CH_3) = 72$ kcal mol^{-1} than a triphenylmethyl radical from triphenylmethane $D(Ph_3C–H) = 75$ kcal mol^{-1}: thus toluene probably arises from compound (10) by homolytic cleavage of the $CH_2–CH_2$ bond. [However, compound (22g) which also contains a *N*-phenethyl group gives ethylbenzene and not toluene—hence this simple explanation may not be wholly correct].

TABLE 2

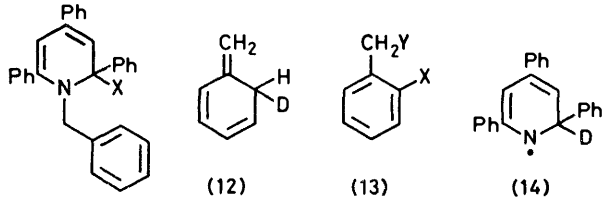
^1H N.m.r. and ^{13}C n.m.r. data for 1,6-disubstituted 2,4-diphenyl-1,2-di- and 1,2,3,6-tetra-hydropyridines (8a, b), (9b), (10), (11a, b) [a]

Spectrum	Comp. no.	Undefined substituents: 6-	1-	Aromatic H or C	Di- or tetra-hydropyridine ring: 2	3	5	N-CH_2 [b]		Aliphatic H or C
^1H	(8a)	Ph	n-C_8H_{17}	7.7—7.2 (15 H, m)	3.5 (1 H, d, *J* 6 Hz)	5.15 (1 H, d, *J* 6 Hz)	5.6 (1 H, s)	3.10 (1 H, m)	2.6 (1 H, m)	1.20—0.7 (15 H, m)
^1H	(8b)	But	n-C_8H_{17}	7.7—7.2 (10 H, m)	3.55 (1 H, d, *J* 6 Hz)	5.41 (1 H, d, *J* 6 Hz)	5.6 (1 H, s)	3.10 (1 H, m)	2.6 (1 H, m)	1.10—0.8 (24 H, m)
^1H	(9b)	Ph	$ClC_6H_4CH_2CH_2$(*p*)	6.85 *c*, 7.14 *d*, 7.74 *e*	5.14 (1H, d, *J* 6 Hz)	5.68 (1 H, dd, *J* 6; 1.5 Hz)	5.55 (1 H, d, *J* 1.5 Hz)	3.34 (1 H, sx)	2.74 (m)	2.74 (m)
^1H	(10)	Ph	$PhCH_2CH_2$	6.6—7.5 (m)	4.05 (1 H, dd, *J* 8; 3 Hz)	2.4—2.6 (m)	5.97 (1 H, t, *J* 3; 3 Hz)	2.4—2.6 (m)		2.4—2.6 (m)
^1H	(11a)	Ph	$PhCH_2$	7.4—7.1 (20 H, m)		5.48 (1 H, ss)	5.57 (1 H, ss)	3.98 (1 H, d, *J* 15 Hz)	4.45 (1 H, d, *J* 15 Hz)	
^1H	(11b)	Ph	$PhCH_2$	7.4—7.1 (20 H, m)	5.02 (1 H, d, *J* 6 Hz)	5.47 (1 H, dd, *J* 6 Hz)	5.52 (1 H, ss)	3.96 (1 H, d, *J* 15 Hz)	4.45 (1 H, d, *J* 15 Hz)	
^{13}C	(10)	Ph	$PhCH_2CH_2$	125—130	65,16 (d*f*)	38.50 (t*f*)	38.50 (t*f*)	52.38 (t*f*)		29.43 (t*f*)
^{13}C	(11a) [h]	Ph	$PhCH_2$	125.7—147.0	60.2 (t*f*)	102.5 (d*f*)	112.2 (d*f*)	54.6 (t*f*)		
^{13}C	(11b) [i]	Ph	$PhCH_2$	125.8—147.1	60.3 (d*f*)	102.6 (d*f*)	112.4 (d*f*)	54.7 (t*f*)		

[a] Spectra determined in $CDCl_3$ with $SiMe_4$ as internal standard. s = Singlet, d = doublet, t = triplet, sx = sextet, m = multiplet, ss = finely split singlet, dd = finely split doublet. [b] Where two peaks are shown, CH_2 is diastereotopic. [c] (2 H, d, *J* 9 Hz). [d] (2 H, d, *J* 9 Hz). [e] (10 H, m). [f] Spin multiplicity off-resonance. [g] 6-Position carbon signal at 62.18 (d). [h] 2 800 Transients. [i] 100 Transients.

A radical process presumably also accounts for the presence of toluene in the thermolysate of dihydropyridine (9b). Brett and Gold [9] observed a radiation-induced displacement of halogen atoms from the halogenobenzenes PhCl, PhBr, and PhI by hydrogen (tritium) atoms, alternatively the toluene from (9b) may arise from one of the ring phenyl groups by a complex ring-opening rearrangement sequence.

Mechanistic Elucidation of the Thermal Cleavage of 1-Benzyl-1,2-dihydro-2,4,6-triphenylpyridine.— Thermal cleavage of compound (11a) *via* a concerted cyclic



(11) (12) (13) (14)

(11) a; X = D b; X = H

(13) a; X = D, Y = H b; X = H, Y = D

mechanism and intermediate (12) should yield a mixture of *o*- and ω-deuteriotoluenes (13a) and (13b) respectively, with a relative ratio (13a) : (13b) $\geqslant 1$, allowing for the primary isotope effect. In contrast, homolysis to give (14) and a benzyl radical should yield triphenylpyridine and ω-deuteriotoluene (13b) uncontaminated by the *o*-deuterio-isomer as the hydrocarbon product.

Reduction of 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (7f) with sodium borodeuteride in methanol–acetonitrile (1 : 1) gave the 2-deuteriodihydropyridine (11a) admixed with 30% of the protio-derivative (11b). The incomplete labelling was detected by the doublet at δ 5.02, corresponding to 2-H in the ^{1}H n.m.r. spectrum (Table 2) and is caused by exchange of the deuteron with a proton from methanol. When the reduction was effected in methan[^{2}H]ol–acetonitrile (1 : 1), dihydropyridine (11a) was isolated in 75% yield and characterised by its elemental analysis, and ^{1}H n.m.r. and ^{13}C n.m.r. spectra (see Table 2). In the ^{13}C n.m.r. spectrum of dihydropyridine (11a), the C-2 triplet centred at δ 59.8 ($J \neq 21$ Hz) is of low intensity: 2 800 transients were necessary to make it become apparent while only 100 transients were sufficient to give to the C-2 in compound (11b) an absorption of intensity comparable with other signals of the spectrum. Spin-lattice relaxation proceeds *via* dipole–dipole relaxation which varies as the magnetogyric ratio of the nucleus causing relaxation.[10] Deuterons have a magnetogyric ratio 6.5 times smaller than protons [11] and therefore are less able to relax the neighbouring carbon atom, hence the low intensity of the triplet. A singlet at δ 60.2 superimposed on the triplet, indicates the presence of traces of dihydropyridine (11b) mixed with (11a).

Thermolysis of the 2-deuterio-1,2-dihydropyridine (11a) gave ω-deuteriotoluene with *ca.* 20% of toluene as shown by ^{1}H n.m.r. integration. The ^{1}H n.m.r. spectrum showed a singlet for CH_3 δ 2.27 and a triplet

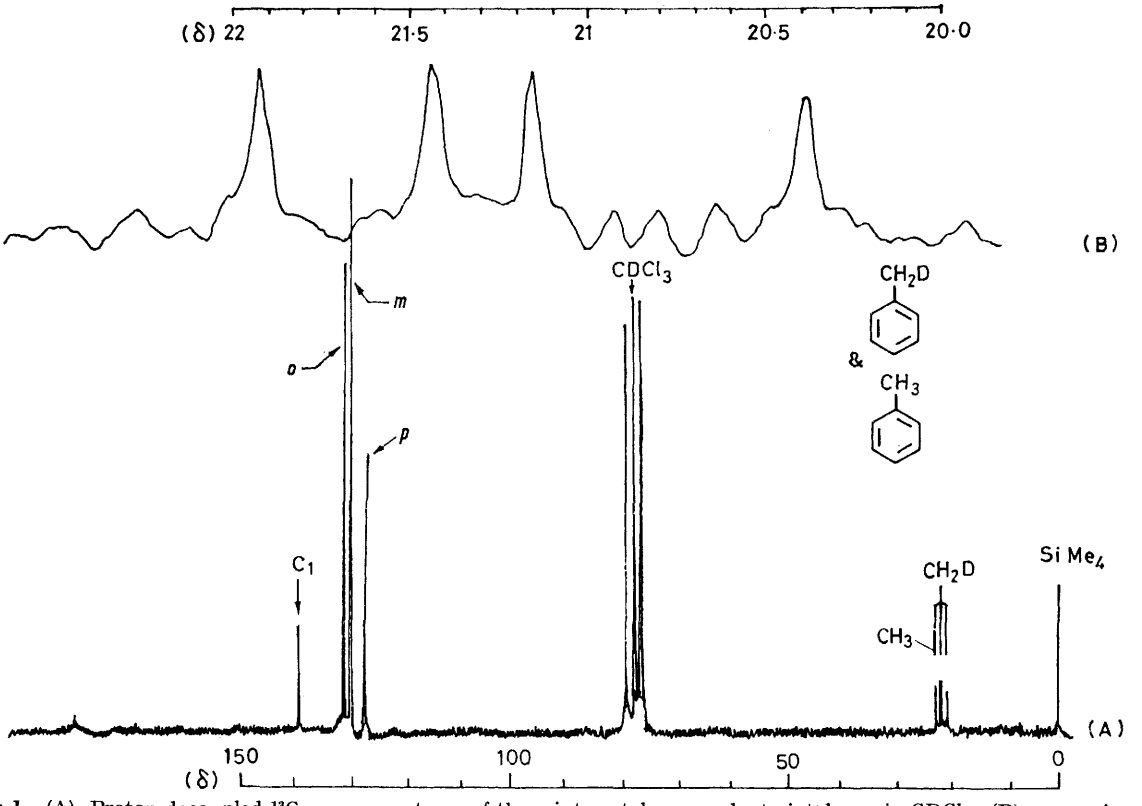


FIGURE 1 (A), Proton-decoupled ^{13}C n.m.r. spectrum of the mixture toluene–ω-deuteriotoluene in $CDCl_3$; (B), expansion of the aliphatic region of (A)

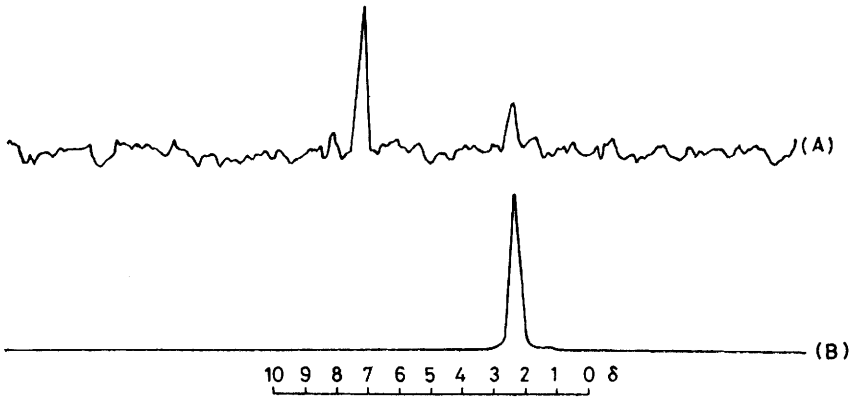


FIGURE 2 (A), Proton-decoupled ^2H n.m.r. spectrum of toluene in CCl_4: 400 transients; (B), proton-decoupled ^2H n.m.r. spectrum of the mixture toluene–ω-deuteriotoluene in CCl_4: 146 transients

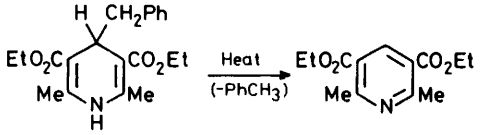
($J \neq 2.5$ Hz) at δ 2.25 for CH_2D (*cf.* $^2J_{H-D}$ 2.03 Hz in 2-deuterioethyl bromide [12]). The proton decoupled ^{13}C n.m.r. spectrum displayed a singlet at δ 21.44 (CH_3) and a triplet at δ 21.15 ($J \neq 19$ Hz) (CH_2D) in the aliphatic and four singlets (*ipso*, *o*-, *m*-, and *p*-carbon atoms) in the aromatic region (Figure 1).

These spectral data provide strong evidence for the radical mechanism: however a concerted rearrangement is still conceivable if the 20% of toluene responsible for a CH_3 absorption in both ^1H and ^{13}C n.m.r. spectra contains deuterons attached to the ring. If deuterons were attached to the ring, the carbon atoms linked to the deuterons should be detectable as a triplet near δ 129 in a ^{13}C n.m.r. spectrum. No triplet was detected around δ 129, even after 2 800 transients: but it would be of low intensity because such carbon atoms comprise only 20% of the total and will possess long relaxation times.

A definite conclusion was provided by the deuterium n.m.r. of the thermolysis mixture. Deuteron chemical shifts are similar to proton chemical shifts.[12] Accordingly, a triplet ($J \neq 2.14$ Hz) centred at δ 2.26 in the ^2H n.m.r. spectrum was attributed to the deuteron coupled with the two protons in the CH_2D group: on irradiation at the proton frequency, the triplet collapsed into a singlet. Most importantly, no deuterons were found to resonate at δ 7.08 (Figure 2). This rules out an electrocyclic thermal fragmentation of 1-benzyl-1,2-dihydro-2,4,6-triphenylpyridine. The relative ease of thermolysis parallels the bond dissociation energies of analogous compounds of the type $R–CH_3$.[8] Thus, the 1-benzyl derivative (11b) affords the corresponding hydrocarbon and triphenylpyridine in good yield [$D(PhCH_2–CH_3)$ = 72 kcal mol^{-1}], whereas the n-octyl derivative gave poor yields of n-octane [$D(Et–CH_3)$ = 85 kcal mol^{-1}], and 1-aryl-1,2-dihydro-2,4,6-triphenylpyridines are thermally stable at *ca.* 200 °C [$D(Ph–CH_3)$ = 93 kcal mol^{-1}].[3,8]

Evidently aromaticity loss on formation of methylenecyclohexadiene is too great. Such an energy barrier does not exist in the *N*-allyl derivative and we plan to investigate the thermal cleavage of 1-(but-2-enyl)-1,2-dihydro-2,4,6-triphenylpyridine.

Preparation of 1,4-Dihydropyridines.—As the thermolysis of *N*-benzyl-1,2-dihydro-2,4,6-triphenylpyridine was initially thought to proceed *via* a 1,5-shift, the elaboration of a molecule in which a 1,5-hydrogen shift was possible without involving a π-bond in the *N*-substituent was sought. 1,4-Dihydropyridines satisfy these criteria and aromatisation of 1,4-dihydropyridine derivatives has been reported *e.g.* (15) ⟶ (16).[13]



(15) (16)

Sodium dithionite reduces simple pyridinium salts to 1,4-dihydropyridines:[14] however, dithionite reduction of 2,4,6-triphenylpyridinium salts gave complex mixtures.[7] The orientation of the borohydride reduction of pyridinium salts depends on steric factors and 1,4-dihydropyridines often occur as by-products.[15]

We planned to direct borohydride attack to the 4-position. 2,6-Diphenylpyrylium perchlorate [16] was prepared from triethyl orthoformate and acetophenone, but on reaction with aniline or benzylamine ring-opening occurred without reclosure to pyridinium: the 4-phenyl ring evidently produces some s-*cis* configuration of the open-chain intermediate favouring ring-reclosure.

2,3,5,6-Tetraphenylpyrylium cation (18) was prepared as the perchlorate (18a) following Simalty *et al.*[17] from deoxybenzoin and formaldehyde followed by ring closure with triphenylmethyl perchlorate in 67% yield (Scheme 2). For large-scale work analogously prepared novel tetrafluoroborate (18b) was preferred. ^1H N.m.r. spectra of salts (18a) and (18b) display a singlet at δ 8.80 and 8.85, respectively, for the 4-proton. Ammonia readily converted salt (18a) into the corresponding pyridine derivative (19).[17]

Salts (18a) and (18b) readily give the corresponding pyridinium salts with primary carbinylamines (Table 3) in ethanol at 25 °C, the reaction is completed in 3 h

TABLE 3

Preparation of 1-substituted 2,3,5,6-tetraphenylpyridinium salts (21)

Comp. no.	1-Substituent	Anion	Conditions for preparation: Solvent	Time (h)	Temp (°C)	Recryst. solvent	Yield (%)	Crystal form [a]	M.p. (°C)	Found C	Found H	Found N	Formula	Required C	Required H	Required H
(21a)	n-C_6H_{13}	BF_4	EtOH	2.5	25	MeCN–Et_2O	83	M	186—189	75.1	6.3	2.6	$C_{35}H_{34}BF_4N, \frac{1}{4}H_2O$	75.1	6.2	2.5
(21b)	n-C_7H_{15}	BF_4	EtOH	2.5	25	MeCN–Et_2O	82	M	98—102	75.9	6.2	2.6	$C_{36}H_{36}BF_4N$	75.9	6.3	2.5
(21c)	n-C_8H_{17}	BF_4	EtOH	12	25	EtOH	65	P	92—95	76.2	6.5	2.5	$C_{37}H_{38}BF_4N$	76.2	6.5	2.4
(21d)	$PhCH_2$	BF_4	EtOH	12	25	EtOH	72	P	155—160	77.1	5.1	2.5	$C_{36}H_{28}BF_4N$	77.0	5.0	2.5
(21e)	$PhCH_2$	ClO_4	EtOH	12	25	EtOH	66	N	162	75.0	5.1	2.3	$C_{36}H_{28}ClNO_4$	75.3	4.9	2.4
(21f)	$ClC_6H_4CH_2(p)$	BF_4	EtOH	5	25	MeCN–Et_2O	86	P	222—224	71.6	4.5	2.2	$C_{36}H_{27}ClBF_4N, \frac{1}{2}H_2O$	71.5	4.7	2.3
(21g)	$PhCH_2CH_2$	BF_4	EtOH	1	25	MeCN–Et_2O	95	P	294—297	76.2	5.7	2.5	$C_{37}H_{30}BF_4N, \frac{1}{2}H_2O$	76.0	5.3	2.4
(21h)	Ph	BF_4	EtOH	3	25	MeCN–Et_2O	82	P	302—303	76.3	4.8	2.6	$C_{35}H_{26}BF_4N, \frac{1}{4}H_2O$	76.1	4.8	2.5
(21i)	2-Pyridyl	BF_4	EtOH	4	78	EtOAc–Et_2O	98	P	225	72.5	4.7	5.0	$C_{34}H_{25}BF_4N_2, H_2O$	72.1	4.8	4.9
(21j)	Pyrimidin-2-yl	BF_4	EtOH	3	78	MeCN–Et_2O	76	M	307—310	71.8	4.4	7.7	$C_{33}H_{24}BF_4N_3, \frac{1}{4}H_2O$	71.6	4.4	7.6

[a] M denotes microcrystals; P, prisms; and N, needles.

TABLE 4

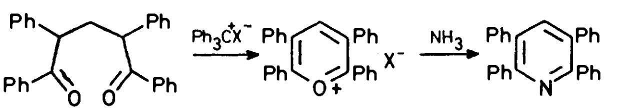
Preparation of 1-substituted 1,4-dihydro-2,3,5,6-tetraphenylpyridines (22)

Compound no.	1-Substituent	Crystallisation solvent	Yield (%)	Crystal form [a]	M.p.[b] (°C)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(22a)	n-C_6H_{13}	[c]	63	M	114—118							
(22c)	n-C_8H_{17}	MeCN	83	P	70—72d	88.8	7.7	2.8	$C_{37}H_{39}N, 0.25\,H_2O$	88.5	7.9	2.8
(22d)	$PhCH_2$	EtOH	72	P	124—125d	90.6	6.1	2.8	$C_{36}H_{29}N$	90.9	6.1	2.8
(22f)	$ClC_6H_4CH_2(p)$	[c]	80	P	145d							
(22g)	$PhCH_2CH_2$	MeCN	60	M	168—170	90.6	6.3	2.5	$C_{37}H_{31}N$	90.8	6.4	2.9
(22h)	Ph	MeCN	92	N	210—211	90.9	6.2	2.9	$C_{35}H_{27}N$	91.1	5.9	3.0
(22i)	2-Pyridyl	MeCN	76	N	200—203	88.7	5.7	6.2	$C_{34}H_{26}N_2$	88.3	5.7	6.1
(22j)	Pyrimidin-2-yl	MeCN	85	M	187			9.0	$C_{33}H_{25}N_3$			9.1

[a] M denotes micro-crystals; P, prisms; and N, needles. [b] d denotes melting with decomposition. [c] Crude product utilised in the pyrolysis.

instead of the ⩾6 h for the triphenyl series. (An even bigger acceleration occurs in the pentaphenyl series: 15 min is an average reaction time.[18]) Salt (18b) with secondary carbinylamines gave only the ethanolysis product (20), previously reported by Basselier.[19]

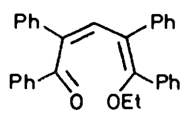
Salts (21a, c, d, f—k) were reduced by sodium borohydride selectively in the 4-position yielding the corresponding 1,4-dihydropyridines (22a, c, d, f—k) (Table 4) as shown by spectra and microanalysis. In particular, all the ^1H n.m.r. spectra displayed a 2 H singlet near δ 3.9 for the two equivalent 4-position methylene protons. U.v. spectroscopy was, before the advent of ^1H n.m.r. spectroscopy, frequently used for distinguishing 1,4-dihydropyridines (two absorption maxima, at 200—240 nm and at 300—400 nm) from the 1,2- and 1,6-isomers (a third band at 250—300 nm).[14] Compounds (22c, d, h, i) are exceptions to this general observation (see Table 5). The 1,4-dihydro-2,3,5,6-tetraphenylpyridines (22a, c, d, f, g), carrying an N-substituent attached to an sp^3 hybridised carbon atom, thermolyse smoothly at ca. 200 °C *in vacuo* to give the hydrocarbon and tetraphenylpyridines (19). By contrast, the N-aryl- and N-heteroaryldihydropyridines (22h, i, j) required temper-



(17) (18) (19)

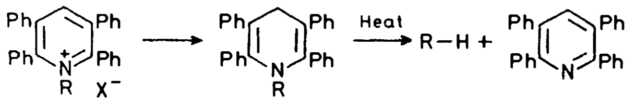
a; X = ClO_4

b; X = BF_4



(20)

SCHEME 2



(21) (22) (19)

R	X	R	X
a; n-C_6H_{13}	BF_4	g; $PhCH_2CH_2$	BF_4
b; n-C_7H_{15}	BF_4	h; Ph	BF_4
c; n-C_8H_{17}	BF_4	i; 2-Pyridyl	BF_4
d; $PhCH_2$	BF_4	j; Pyrimidin-2-yl	BF_4
e; $PhCH_2$	ClO_4	k; $ClC_6H_4(p)$	BF_4
f; $ClC_6H_4CH_2(p)$	BF_4	l; 3-Picolyl	BF_4

TABLE 5

Electronic absorption data for 1,4-dihydropyridines (22c, d, h, i)

No.	R	$\lambda_{max.}$/nm (ε)			
(22c)	n-C_8H_{17}	230 (35 800)	273 (35 300)	322 (17 900)	350 (13 400)
(22d)	$PhCH_2$	225 (21 900)	275 (18 100)	315 (9 000)	350 (6 200)
(22h)	Ph	227 (26 800)	266 (22 200)	303 (13 800)	337 (8 900)
(22i)	2-Pyridyl	225 (23 800)	262 (21 900)	310 (13 400)	345 (7 800)

atures higher than 300 °C to release the aromatic hydrocarbon (see Table 6). Compound (22h) was recovered unchanged after 2 h at 230 °C.

TABLE 6

Thermolysis and pyrolysis of 1,4-dihydropyridines (22a, c, d, f—j)

Starting material No.	R	Temp. (°C)	Time (h)	Product [a]	Yield (%)
(22a)	n-C_6H_{13}	180	4	n-Hexane	58
(22c)	n-C_8H_{17}	180	4	n-Octane	88
(22d)	$PhCH_2$	200	5	Toluene	44
(22f)	$ClC_6H_4CH_2$(*p*)	220	2	4-Chlorotoluene	62
(22g)	$PhCH_2CH_2$	180	2	Ethylbenzene	64
(22h)	Ph	230	2		*b*
(22h)	Ph	>300	0.5	Benzene	54
(22i)	2-Pyridyl	>300	0.5	Pyridine	*c*
(22j)	Pyrimidin-2-yl	>300	2	Pyrimidine	26

[a] All hydrocarbons were identified by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples. [b] Starting material recovered unchanged. [c] Product was contaminated and could not be purified.

Conclusion.—1,4-Dihydropyridines of type (22) are intermediates of a wider scope in deamination than the previously reported [3] 1,2-dihydropyridines: not only benzylic, but also aliphatic and even aromatic amines can be converted into the respective hydrocarbons. The limits to this transformation are two-fold: in the aliphatic series to primary carbylamines and in the aromatic series by the high temperatures.

EXPERIMENTAL

M.p.s are uncorrected and were measured on a Reichert microscope hot stage. I.r. and 60 MHz and 100 MHz ^1H n.m.r. spectra were recorded on a Perkin-Elmer 257 grating i.r. spectrometer, R 12 Perkin-Elmer n.m.r. spectrometer, and HA-100 Varian n.m.r. spectrometer respectively. 15.4 MHz Deuterium and 25.05 MHz ^{13}C n.m.r. measurements were done on a FX-100 JEOL instrument, u.v. on a SP800 Unicam, and mass spectra on a RMU-6E Hitachi Perkin-Elmer spectrometer. G.l.c. analyses were performed with a Perkin-Elmer F 11 gas chromatograph (flame ionisation; stationary phase of Chromosorb 20M; oven temperatures 180—200 °C unless otherwise stated). N.m.r. measurements used $SiMe_4$ as internal standard.

The following compounds were made by the literature methods indicated: 2,4,6-triphenylpyrylium tetrafluoroborate,[20] m.p. 249—250 °C (lit.,[20] m.p. 253—255 °C), 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (7f),[21] m.p. 190—192 °C (lit.,[21] m.p. 196—197 °C), 2-t-butyl-4,6-diphenylpyrylium perchlorate,[4,22] m.p. 261—262 °C (lit.,[4] m.p. 264—266 °C), 2-t-butyl-4,6-diphenylpyridine,[4] m.p. 88—89 °C (lit.,[4] m.p. 87—88 °C), 1-benzyl-1,2-dihydro-2,4,6-triphenylpyridine (11b),[3a] m.p. 105 °C (lit.,[3a] m.p. 97—100 °C), 2,3,5,6-tetraphenylpyrylium perchlorate,[17a] m.p. 310 °C (lit.,[17a] m.p. 315 °C), 2,3,5,6-tetraphenylpyridine (19) (as for 2-t-butyl-4,6-diphenylpyridine [4]), m.p. 229—230 °C (lit.,[17a] m.p. 241 °C), 2,6-diphenylpyrylium perchlorate, m.p. 222—223 °C, (lit.,[16] m.p. 222—223 °C), and 1,3-dibenzoyl-1,3-diphenylpropane (17) [17b] m.p. 147—149 °C (lit.,[17b] m.p. 145.5—146.5 °C).

Preparation of 2,4,6-*Triphenyl- and* 2-*t-Butyl*-4,6-*diphenyl-pyridinium Salts* (7).—To 2,4,6-triphenylpyrylium tetrafluoroborate (15 g, 0.037 9 mol) under absolute EtOH (60 ml) was added the amine (0.037 9 mol) and the mixture was stirred at 25 °C for 12 h. Et_2O (100 ml) was added and the precipitated *salt* recrystallised (see Table 1).

1,2-*Dihydro*-1-*n-octyl*-2,4,6-*triphenylpyridine* (8a).—$NaBH_4$ (0.45 g, 0.011 8 mol) was added gradually to salt (7c) (6 g, 0.011 8 mol) in MeOH–MeCN 1 : 1 (6 ml) at 0 °C. The mixture was stirred for a further hour at 0—5 °C. The solvent was removed at 30 °C and 20 mmHg and Et_2O (30 ml) was added. The inorganic material was filtered off and the filtrate was evaporated at 20 mmHg. The residue was a yellow *oil* (2.6 g, 54%) which decomposed on standing: δ($CDCl_3$, 60 MHz) 1.15 (15 H, m), 2.6 (1 H, m), 3.1 (1 H, m), 3.5 (1 H, d, *J* 6 Hz), 5.15 (1 H, d, *J* 6 Hz), 5.6 (1 H, s), and 7.4 (15 H, m).

2-*t-Butyl*-1,2-*dihydro*-1-*n-octyl*-4,6-*diphenylpyridine* (8b) was prepared similarly to compound (8a) and was obtained as a yellow *oil* (87%) which decomposed on standing; $\nu_{max.}$ (neat) 3 040m, 3 020m, 2 960s, 2 940s, 2 840s, 1 640m, 1 580w, 1 550s, 1 460s, 1 420w, 1 390m, 1 360s, 1 340w, 1 300w, 1 220w, 1 190w, 1 140s, 1 070s, 1 020m, 1 000m, 910w, 890w, 830w, 760s, and 690s cm^{-1}; δ($CDCl_3$, 60 MHz) 1.0—1.2 (24 H, m), 2.60 (1 H, m), 3.1 (1 H, m), 3.55 (1 H, d, *J* 6 Hz), 5.41 (1 H, d, *J* 6 Hz), 5.6 (1 H, s), and 7.4 (10 H, m).

1-[2-(4-*Chlorophenyl*)*ethyl*]-1,2-*dihydro*-2,4,6-*triphenylpyridine* (9b) was prepared as for dihydropyridine (8a) and was obtained as a yellow unstable *oil* (68%), b.p. 30 °C at 20 mmHg, characterised spectrally; $\nu_{max.}$ (CHBr) 3 070m, 3 040s, 2 960m, 2 900m, 2 860m, 1 630m, 1 600s, 1 580m, 1 550s, 1 490s, 1 450s, 1 410m, 1 350m, 1 300m, 1 250w, 1 200w, 1 090s, 1 070s, 1 030m, 1 010s, 910m, 840m, 810s, 740s, and 690s cm^{-1}; δ($CDCl_3$, 60 MHz) 2.74 (3 H, m), 3.34 (1 H, dt, J_1 14 Hz, $J_2 = J_3 = 6$ Hz), 5.14 (1 H, d, *J* 6 Hz), 5.55 (1 H, s), 5.68 (1 H, d, *J* 6 Hz), 6.85 (2 H, d, *J* 9 Hz), 7.14 (2 H, d, *J* 9 Hz), and 7.34 (15 H, m).

1,2,3,6-*Tetrahydro*-1-(2-*phenylethyl*)-2,4,6-*triphenylpyridine* (10) was prepared as for the dihydropyridine (8a). It crystallised from Me_2CO as *needles* (20%), m.p. 173—175 °C (decomp.) (Found: C, 89.7; H, 7.2; N, 3.4. $C_{31}H_{29}N$ requires C, 89.6; H, 7.0; N, 3.4%); $\nu_{max.}$ ($CHBr_3$) 2 910m, 2 860w, 1 600m, 1 490s, 1 450s, 1 380w, 1 300m, 1 070m, 1 020m, 970w, 900w, 870s, 800w, 760s, and 750s cm^{-1}; δ($CDCl_3$, 100 MHz) 2.4—2.6 (6 H, m), 4.05 (1 H, dd, J_1 8 Hz, J_2 3 Hz), 4.58 (1 H, dd, J_1 3 Hz, J_2 2 Hz), 5.97 (1 H, t, J_1 8 Hz, J_2 3 Hz), 4.58 (1 H, dd, J_1 3 Hz, J_2 2 Hz), 5.97 (1 H, t, $J_1 = J_2 = 3$ Hz), and 6.6—7.5 (20 H, m); *m/e* (70 eV) 77 (8), 79 (4), 91 (65), 92 (5), 103 (8), 105 (14), 115 (9), 117 (22), 118 (78), 119 (11), 128 (2), 129 (3), 191 (4), 219 (18), 220 (3), 231 (3), 323 (100), 324 (36), 325 (6), 337 (2), 414 (8), 415 (8), and 416 (3%).

1-*Benzyl*-2-*deuterio*-1,2-*dihydro*-2,4,6-*triphenylpyridine* (11a).—$NaBD_4$ (0.43 g, 0.010 3 mol) was gradually added during 30 min with stirring at 0 °C to 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (7f) (5 g, 0.010 3 mol) in MeCN–CD_3OD 1 : 1 (20 ml). Stirring was continued for 2 h at 0 °C. *Dihydropyridine* (11a) crystallised out as yellow prisms (EtOH) (3.1 g, 75%), m.p. 112—113 °C (decomp.) (Found: C, 89.5; H and D, 6.3; N, 3.6. $C_{30}H_{24}DN,0.25H_2O$ requires C, 89.2; H and D, 6.4; N, 3.5%); $\nu_{max.}$ ($CHBr_3$) 3 050m, 2 900w, 2 840w, 1 630m, 1 600m, 1 590w, 1 550s, 1 490s, 1 450s, 1 420s, 1 360s, 1 290w, 1 230w, 1 220w, 1 200w, 1 070s, 1 020m, 1 010w, 970m, 880w, 820w, 770s, 740s, 720s, and 690s cm^{-1}; δ($CDCl_3$, 100 MHz) 3.98 (1 H, d, *J* 15 Hz), 4.46 (1 H, d, *J* 15 Hz), 5.48 (1 H, s, *J* 2 Hz), 5.47 (1 H, s, *J* 2 Hz), and 7.1—7.5 (20 H, m).

Thermolysis of Tetra- and Di-hydropyridines.—The tetra- and di-hydropyridines were dried at 50 °C at 0.5 mmHg or 20 °C at 0.5 mmHg for solids and oily liquids respectively. They were then heated at 0.5 to 1 mmHg at 200—230 °C.

Thermolysis of 1,2-*Dihydro*-1-*n-octyl*-2,4,6-*triphenylpyridine* (8a).—The oily dihydropyridine (8a) (5.2 g, 0.012 4 *mol*) was heated at 1 mmHg in a distillation apparatus at 200—210 °C for 4 h. The liquid trapped at −70 °C was identified as n-octane (0.1 g, 7%) by i.r. and ^{1}H n.m.r. comparison with an authentic sample.

Thermolysis of 2-*t-Butyl*-1,2-*dihydro*-1-*n-octyl*-4,6-*diphenylpyridine* (8b).—When dihydropyridine (8b) was heated at 200 °C for 2 h, n-octane (20%) was isolated as the distillate.

Thermolysis of 1-[2-(4-*Chlorophenyl*)*ethyl*]-1,2-*dihydro*-2,4,6-*triphenylpyridine* (9b).—The oily dihydropyridine (9b) was heated at 200—230 °C for 3 h: *p*-chlorotoluene (27%) and toluene (18%) distilled out.

Thermolysis of 1,2,3,6-*Tetrahydro*-1-(2-*phenylethyl*)-2,4,6-*triphenylpyridine* (10).—The crystalline tetrahydropyridine (10) (1.9 g, 0.004 6 mol) was maintained at 200 °C for 2 h. The distillate was shown to be toluene (0.23 g, 53%) by i.r. and ^{1}H n.m.r. data.

Thermolysis of 1-*Benzyl*-1,2-*dihydro*-2,4,6-*triphenylpyridine* (11b).—Dihydropyridine (11b) kept at 200 °C under 1 mmHg for 2 h gave toluene (70%) characterised by comparison of i.r. and ^{1}H n.m.r. spectra with those of an authentic sample.

2,3,5,6-*Tetraphenylpyrylium Tetrafluoroborate* (18b).—1,3-Dibenzoyl-1,3-diphenylpropane (17) (18.47 g, 0.045 mol) and trityl tetrafluoroborate (15.0 g, 0.045 mol) were refluxed for 1 h in glacial HOAc (60 ml). On cooling, the crystals were filtered off, washed with Et_2O (100 ml), and the *tetrafluoroborate* (18b) crystallised from MeCN as yellow needles (10.5 g, 50%), m.p. 299—300 °C (decomp.) (Found: C, 73.6; H, 4.4. $C_{29}H_{21}BF_4O$ requires C, 73.7; H, 4.5%); $\nu_{max.}$ ($CHBr_3$) 1 600w, 1 570w, 1 500m, 1 460s, 1 430s, 1 380m, 1 050s, 760m, and 680s cm^{-1}; δ(CF_3CO_2H, 60 MHz) 7.53 (20 H, m), and 8.85 (1 H, s).

Preparation of 1-*Substituted* 2,3,5,6-*Tetraphenylpyridinium Salts* (21).—The amine (0.021 2 mol) and 2,3,5,6-tetraphenylpyrylium tetrafluoroborate (18b) (10 g, 0.021 2 mol) were stirred for 3—12 h at 25 °C in absolute EtOH (60 ml). The *pyridinium salt* (21) was filtered off and crystallised (see Table 3).

Preparation of 1-*Substituted* 1,4-*Dihydro*-2,3,5,6-*tetraphenylpyridines* (22).—The 1-substituted 2,3,5,6-tetraphenylpyridinium salt (21) (0.008 7 mol) was dissolved in MeOH–MeCN (1 : 1) (5 ml). $NaBH_4$ (0.033 g, 0.000 87 mol) was added gradually to the stirred solution at 0 °C. The dihydropyridine (22) was filtered off and crystallised (see Table 4).

Thermolysis of 1,4-*Dihydropyridines.*—The 1,4-dihydropyridine was kept at 50 °C at 1 mmHg for 1 h and then heated in a distillation apparatus. The distillate was identified by i.r. and ^{1}H n.m.r. data and comparison with those of an authentic sample (see Table 6).

1-*Ethoxy*-1,2,4,5-*tetraphenylpenta*-1,3-*dien*-5-*one* (20).—(i) The pyrylium salt (18b) (7 g, 0.015 mol), absolute EtOH (60 ml), and cyclohexylamine (1.45 g, 0.015 mol) were stirred at 25 °C for 2 h. Yellow crystals were filtered off. The filtrate was evaporated at 20 mmHg and EtOH added to afford a second crop. Recrystallisation from EtOH gave compound (20) (6.86 g, 83%) as yellow needles, m.p. 157—158 °C (lit.,[19] m.p. 159 °C) (Found: C, 86.3; H, 6.0. Calc. for $C_{31}H_{26}O_2$: C, 86.5; H, 6.1%); $\lambda_{max.}$ (EtOH) 215 (ε 16 600), 238 (16 600), 266 (shoulder, 11 600), and 354 nm (12 600); $\nu_{max.}$ ($CHBr_3$) 1 650m, 1 600m, 1 580m, 1 560m, 1 500s, 1 450s, 1 330w, 1 240m, 1 180s, 1 070s, 1 040m, 1 000m, 990m, 910w, 750s, and 690s cm^{-1}; δ($CDCl_3$, 60 MHz) 1.3 (3 H, t), 3.86 (2 H, q), 6.9 (1 H, s), and 7.25—7.60 (20 H, m); *m/e* (70 eV) 77 (57), 78 (4), 105 (100), 106 (14), 178 (7), 189 (6), 191 (9), 202 (3), 203 (3), 279 (3), 296 (4), 297 (6), 325 (7), 353 (6), 385 (6), 386 (67), 387 (27), 388 (4), 402 (1), 430 (31), and 431 (11%).

(ii) Compound (20) was also obtained by allowing α-methylbenzylamine to react with salt (18b) in the same manner as described above. Compound (20) crystallised from EtOH as yellow needles (71%), m.p. 157—158 °C.

Reaction of the Vinyl Ether (20) *with Fluoroboric Acid.*—Compound (20) (2 g, 0.005 mol) was dissolved in hot EtOH (50 ml). 40% HBF_4 (2.2 g, 0.01 mol) was added dropwise to yield a yellow precipitate which was crystallised from HOAc. It was shown to be the pyrylium salt (18b) (2.2 g, 92%), m.p. 300 °C (decomp.); $\nu_{max.}$ ($CHBr_3$) 1 600w, 1 570w, 1 500m, 1 460s, 1 430s, 1 380m, 1 050s, 760m, and 680s cm^{-1}.

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