Reductive Deamination of Alkyl and Aryl Primary Amines *via* 1,4-Dihydropyridines and a Note on the Mechanism of Reductive Deamination of Benzylamine *via* a 1,2-Dihydropyridine[1]

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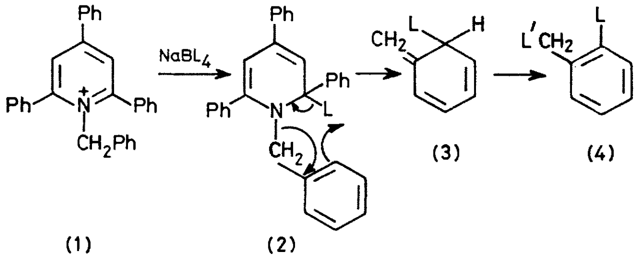
Summary Alkyl- and aryl-amines react with 2,3,5,6-tetraphenylpyrylium cations to yield pyridinium salts which are reduced regiospecifically by $NaBH_4$ to the 1,4-dihydropyridines which thermolyse at 180—200 °C (for the alkyl derivatives) to give the corresponding alkanes in synthetically useful overall yields (some aryl derivatives thermolyse at 300 °C to give the corresponding arenes); ^2H n.m.r. spectroscopy is used to demonstrate the radical nature of the thermolysis of 1-benzyl-2,4,6-triphenyl-1,2-dihydropyridine.



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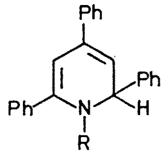

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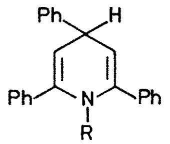

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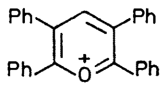

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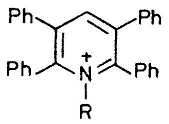

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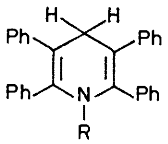

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We have shown[2] that allylamines, benzylamines, and heteroarylmethylamines can be reductively deaminated by a three-step process: (i) conversion by triphenylpyrylium cation into the pyridinium salt, (ii) reduction by borohydride to the 1,2-dihydropyridine [*cf.* (**1**) → (**2**)], and (iii) pyrolysis. Pyrolysis of similar 1,2-dihydropyridines (**5**) derived from alkylamines or arylamines failed.[3] We initially attributed this to the possibility of allowed electrocyclic reactions [*cf.* (**2**) → (**3**)] for the former class, but not the latter. Attention was therefore directed to the preparation of 1,4-dihydropyridines for which electrocyclic elimination of an *N*-alkyl or *N*-aryl substituent should be easier.

Attempts to prepare 1,4-dihydropyridines (**6**) in good yield from 2,4,6-triphenylpyridinium salts having failed,[3b] we resorted to steric direction[4] of the attack by borohydride

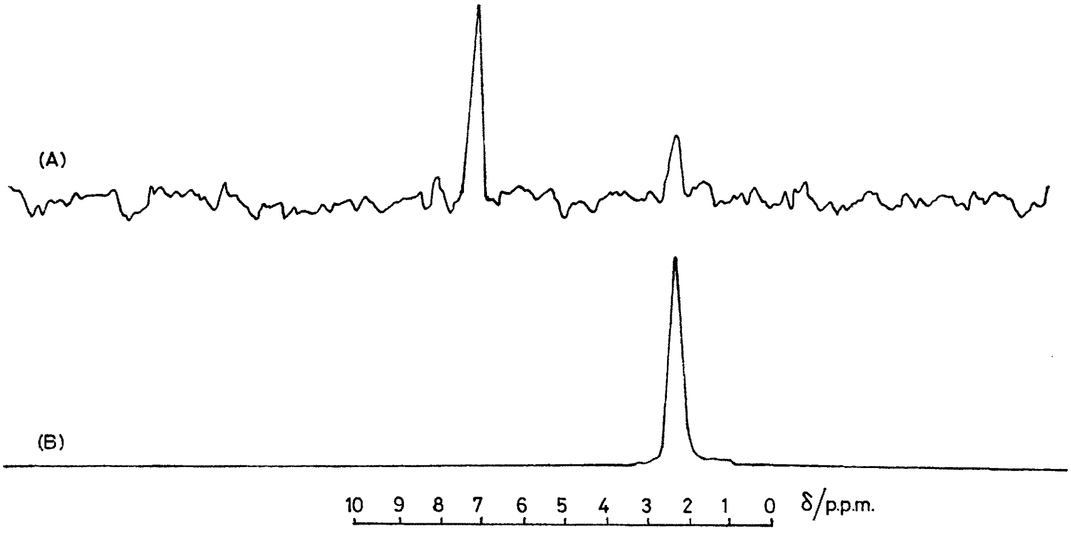

Figure. (A) Proton-decoupled ^2H n.m.r. spectrum of toluene (natural abundance of ^2H) (400 transients and high gain), and (B) proton-decoupled ^2H n.m.r. spectrum of ω-deuteriotoluene from pyrolysis of 1-benzyl-2-deuterio-2,4,6-triphenyl-1,2-dihydropyridine [(**2**); L = D] (146 transients and low gain).

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† Satisfactory analytical data were obtained for all new compounds reported.

to the 4-position. 2,3,5,6-Tetraphenylpyrylium tetrafluoroborate (**7**) reacts readily with a series of amines to yield the pyridinium salts (**8**); the n-hexyl, n-heptyl, n-octyl, benzyl, *p*-chlorobenzyl, phenyl, *p*-chlorophenyl, 2-pyridyl, and 2-pyrimidinyl derivatives were prepared† in an average yield of 80%.

The tetraphenylpyridinium fluoroborates (**8**) were smoothly reduced by sodium borohydride to the corresponding 1,4-dihydropyridines (**9**); the structures were confirmed by analysis and by spectral data,[3b] in particular all displayed in the ^{1}H n.m.r. spectrum a singlet for two hydrogen atoms near δ 3·9 attributed to the two equivalent CH_2 protons of the 4-position of the ring. The average yield for the nine 1,4-dihydropyridines prepared was 71%.

On pyrolysis at 180—200 °C, the compounds in which the 1-substituent was attached by an sp^3-hydridised carbon thermolysed smoothly to give 2,3,5,6-tetraphenylpyridine and the corresponding hydrocarbon in the yields indicated: n-hexane (58%), n-heptane (52%), n-octane (88%), toluene (44%), *p*-chlorotoluene (62%), and ethylbenzene (64%). Thermolysis of the 1-aryl and 1-heteroaryl derivatives required a temperature of 300 °C to give benzene (54%) and pyrimidine (26%).

Although the development of the foregoing synthetic route was a result of the postulation of the electrocyclic mechanism (**2**) $\rightarrow$ (**3**) [$\rightarrow$(**4**)], we now know that this route is incorrect, at least for the pyrolysis of 1-benzyl-2,4,6-triphenyl-1,2-dihydropyridine (**2**). Reduction of the pyridinium salt (**1**) with $NaBD_4$ gave the 2-deuterio-derivative [(**2**); L = D] which pyrolysed to give monodeuteriotoluene. The electrocyclic mechanism should give appreciable quantities of both side-chain [(**4**); L = H, L′ = D] and *ortho*-labelled toluene [(**4**); L = D, L′ = H]. However, only the former was present, as was shown by ^{1}H and ^{13}C n.m.r. spectroscopy (see ref. 3b) and, most convincingly, by the ^{2}H n.m.r. spectrum (Figure). This indicates that the reduction proceeds by homolysis of the N–C bond, possibly followed by a radical chain.

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[1] *Cf.* A. R. Katritzky, A. M. El-Mowafy, and R. C. Patel, in the series 'Heterocycles in Organic Synthesis,' pt. 29, in preparation.

[2] A. R. Katritzky, J. Lewis, and P.-L. Nie, *J.C.S. Perkin I*, in the press.

[3] (a) P.-L. Nie, Ph.D. Thesis, University of East Anglia, 1977; (b) B. Plau, Ph.D. Thesis, University of East Anglia, 1978.

[4] *Cf.* K. Wallenfels and M. Schülly, *Annalen*, 1959, **621**, 86, 106, 215.