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ALLYLIC AND BENZYLIC DEAMINATION BY THERMAL CLEAVAGE OF 1-SUBSTITUTED 1,2-DIHYDRO-2,4,6-TRIPHENYLPYRIDINES.[1]

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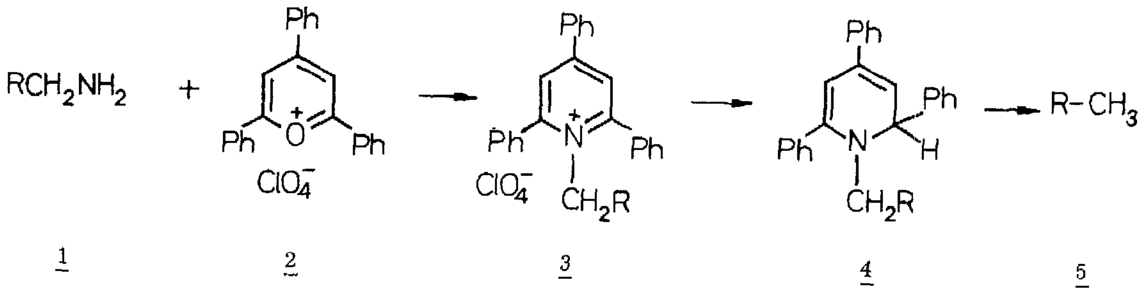
While the conversion $R\text{-}NH_2$ into R-H, via diazotisation and reduction, is a well-known and synthetically important technique in the aromatic series (R = Aryl)[3], comparatively few methods are available to achieve the same result in the aliphatic series[4]. We here describe a three-step process which appears to be generally applicable to the cases in which R is a benzylic or allylic radical. Catalytic (H_2/Pd) and chemical (Na/Hg/H_2O) hydrogenolysis of benzylic and allylic amines and quaternary ammonium salts[5] provide alternative methods, but the present procedure has the feature of specificity for primary amines.

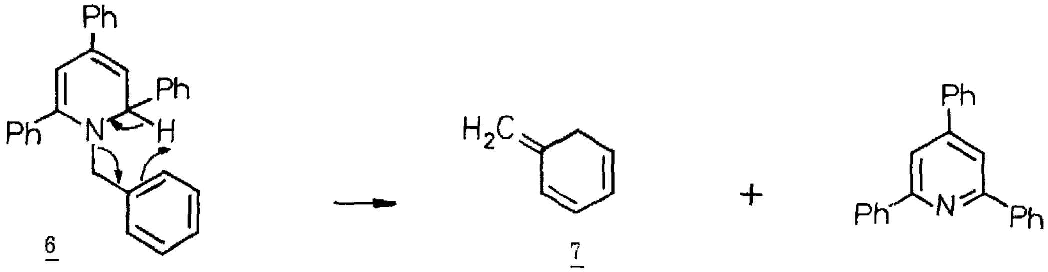
We find that 2,4,6-triphenylpyridinium salts 3, which are readily obtained from the amines 1 and triphenylpyrylium perchlorate 2, are reduced by sodium borohydride in good yield to the dihydro-derivatives 4. These smoothly eliminate 2,4,6-triphenylpyridine on pyrolysis at 200°C in vacuo to give the product 5.[6] Yields and physical data are listed in the Table.

TABLE. PYRIDINIUM SALTS, DIHYDROPYRIDINES, AND THEIR THERMAL CLEAVAGE PRODUCTS

	Salts 3		Dihydropyridines 4		Products 5
R	Yield(%)	M. p. (°C)	Yield(%)	M. p. (°C)	Yield(%)
Vinyl	85	146-148[a]	ca 85	—[b]	81[c]
Phenyl	87	196-198[a]	86	97-100[a]	75[d]
2-Furyl	45	118(dec)[a]	85	—[b]	82[d]
2-Pyridyl	77	226-227[a]	75	127-129[a]	75[d]
4-Pyridyl	80	178 (dec)[a]	85	—[b]	77[d]

Footnotes: [a] Satisfactory analytical and spectral data were obtained for all these new compounds. [b] Unstable oil, not further characterised. [c] Isolated as 1,2-dibromopropane. [d] Identical by spectral comparison with authentic material.





Although the mechanism of formation of the products 5 is as yet undetermined, a plausible route is, as illustrated for the benzyl case (6), via a retro-ene reaction,[7] to form the methylenedihydrobenzene 7, which rearomatises to toluene (5; R = Ph).

REFERENCES AND FOOTNOTES

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(6) In a typical experiment, 2,4,6-triphenylpyrylium perchlorate[8] (13 g, 0.032 mole) and benzylamine (4.3 g, 0.04 mole) were stirred in ethanol (100 ml) for 4 hr, to form the 1-benzyl-2,4,6-triphenylpyridinium salt (3; R = Ph) (13 g). This salt (12 g) was reduced by slow addition of sodium borohydride (0.94 g) to a stirred, cooled (0-5°C) solution in acetonitrile - methanol (1 : 1). After 1 hr the yellow dihydropyridine (4; R = Ph) (8.28 g) was collected and recrystallised from ethanol. After drying, the 1-benzyldihydropyridine (8 g) was heated in a distillation flask to 200°C in vacuo (12 Torr). The evolved gases were condensed in a trap cooled in liquid nitrogen. The distillate proved to be toluene (1.84 g, 75%).

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