Replacement of Primary Amino Groups by Hydrogen *via* Tetrahydrodibenzacridinium Salts

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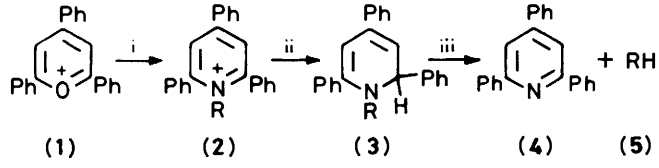
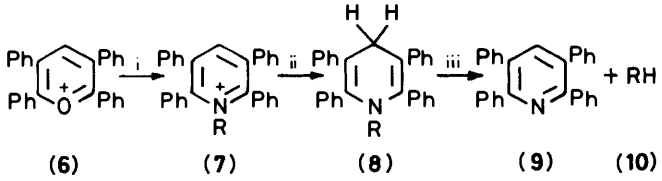
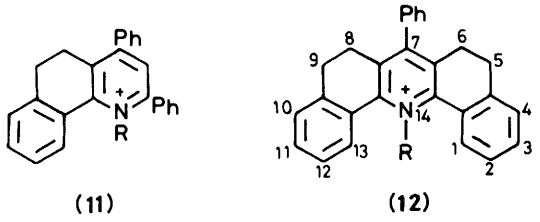
5,6,8,9-Tetrahydrodibenzo[*c,h*]xanthylium salts (**13**) react with amines to yield the corresponding tetrahydroacridinium salts (**14**) which are reduced by $NaBH_4$ to hexahydroacridines (**15**). The *N*-alkylhexahydroacridines undergo thermolysis at *ca.* 160 °C and the *N*-aryl analogues at >250 °C to give alkanes and arenes. The *N*-alkyltetrahydroacridinium salts (**14**) and their 7-phenyl analogues (**12**) react at *ca.* 130 °C with 1,5-diazabicyclo[4.3.0]non-5-ene to give the corresponding alkanes in good yield.

We have previously described three methods for the conversion of primary amino groups into the corresponding hydrogen compounds ($RNH_2 \rightarrow RH$) using pyrylium intermediates. In the first,[1] the amine is converted by 2,4,6-triphenylpyrylium cation (**1**) into the corresponding pyridinium salt (**2**), and reduced by borohydride to the 1,2-dihydropyridine (**3**) which is pyrolysed to afford 2,4,6-triphenylpyridine (**4**) and the hydrocarbon (**5**). The second method[2] utilises the 2,3,5,6-tetraphenylpyrylium salt (**6**), this *via* (**7**) gives the 1,4-dihydropyridine (**8**), which is again pyrolysed to afford (**9**) and (**10**). The third method,[3] involves the pyrolysis of tri- (**11**) and penta-cyclic pyridinium fluorides (**12**).





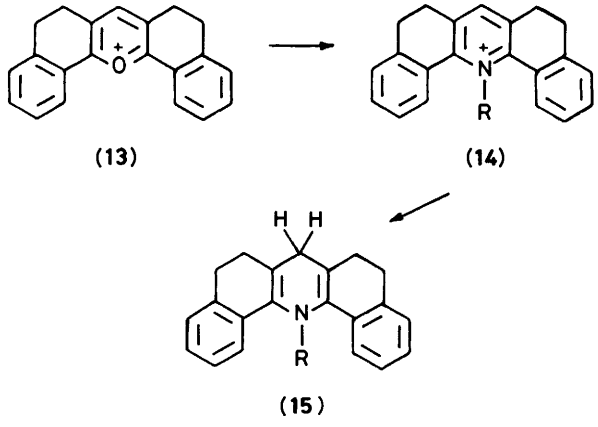


Reagents and conditions: i, RNH_2; ii, $NaBH_4$; iii, Heat

The first method works for allyl-, benzyl-, and heterobenzyl-amines, but dihydropyridines (**3**; R = aryl) are thermally very stable,[1b] whereas (**3**; R = alkyl) yield complex mixtures on pyrolysis.[2b] The second method also succeeds for both R = alkyl and R = aryl, but requires high temperatures, >300 °C for (**8**; R = aryl) and 180—200 °C for (**8**; R = alkyl). The third method is restricted to compounds R = aryl and heteroaryl (alkyl compounds give alkyl fluorides[4]) and utilises temperatures of 130—200 °C.

We have shown that scission of the N–C bond of the *N*-substituent is usually far easier in pentacyclic 5,6,8,9-tetrahydrodibenz[*c,h*]acridinium systems (**12**) than in monocyclic pyridinium cations of types (**2**) or (**7**), because of steric acceleration.[5] The work described in the present paper was originally directed at the preparation of 1,4-dihydropyridines of the pentacyclic system (**12**), but then developed an alternative approach.

Preparation of Tetrahydrodibenzacridinium Salts (**14**) *and Hexahydrodibenzoacridines* (**15**).—2-Hydroxymethylene-3,4-dihydronaphthalen-1(2*H*)-one[6] was treated with 3,4-dihydronaphthalen-1(2*H*)-one and trifluoromethanesulphonic acid to give 5,6,8,9-tetrahydrodibenzo[*c,h*]xanthylium trifluoromethanesulphonate (**13**). Reaction with a series of primary alkyl and aromatic amines gave the corresponding acridinium salts (**14**) (Table 1; analytical data are given in Table 2 which is part of a Supplementary Publication.†). Although the alkyl derivatives (**14a—c**) could not be obtained crystalline, spectral characterisation confirmed their structures.



In the ^1H n.m.r. spectra (Table 3; part of a Supplementary Publication†) the *N*-substituent α-methylene protons of (**14a—c**) appeared as a triplet at δ 5.5 and the remaining *N*-substituent protons as a multiplet at δ 0.5—1.5. In all the compounds (**14a—f**) the methylene ring groups gave a broad singlet at δ 3.0. [The protons at C-1, -7 and -13 in (**14a—c**) appeared as a multiplet at δ 8.5 and the remaining aromatic protons showed as a multiplet

† The material (Tables 2–7) treated as a Supplementary Publication is available as SUP. No. 23970 (7 pp.). For details of the Supplementary Publications Scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

Table 1. Preparation and pyrolysis of 14-substituted 5,6,8,9-tetrahydrodibenz[*c,h*]acridinium trifluoromethanesulphonates (**14**), and 14-substituted 5,6,7,8,9,14-hexahydrodibenz[*c,h*]acridines (**15**)

Compound	*N*-Subst.	Method of Prep.	Yield (%)	M.p. (°C)	Crystal form	Thermolysis		
						Hydrocarbon	Yield (%)	*T* °C
(**14a**)	n-Hexyl	A	85	Oil		n-Hexane	50	*a*
(**14b**)	n-Heptyl	A	90	Oil		n-Heptane	65	*a*
(**14c**)	n-Octyl	A	90	Oil		n-Octane	80	*a*
(**14d**)	Phenyl	B	73	266	Prisms[b]			
(**14e**)	*p*-Tolyl	B	62	261	Plates[b]			
(**14f**)	*p*-$MeOC_6H_4$	B	80	219	Prisms[b]			
(**15a**)	n-Hexyl		90	148	Prisms[b]	n-Hexane	40	165
(**15b**)	n-Heptyl		95	118	Prisms[c]	n-Heptane	65	140
(**15c**)	n-Octyl		95	84	Needles[b]	n-Octane	80	180
(**15d**)	Phenyl		90	226—228	Needles[d]			
(**15e**)	*p*-Tolyl		65	244—247	Prisms[b]			
(**15f**)	*p*-$MeOC_6H_4$		93	218—220	Prisms[e]			

[a] With DBN at 100—140 °C. [b] From EtOH. [c] From MeCN. [d] From CH_2Cl_2–Et_2O. [e] From EtOH–Et_2O

at δ 7.3—7.9. However, the aromatic region in (**14d—f**) disclosed a 1 H singlet at δ 8.3 corresponding to 7-H: in these compounds 1-H and 13-H are evidently shifted upfield by a diamagnetic ring-current effect from the 14-aryl group and therefore coincide with the remaining aromatic protons at δ 6.3—7.6.

The ^{13}C n.m.r. spectra of (**14a—c**) were particularly characteristic for the aliphatic carbon signals (Table 4; part of a Supplementary Publication*). The assignments follow by comparison with the corresponding chemical shifts of the carbon atom of the corresponding n-alcohols.[7]

The 14-substituted 5,6,8,9-tetrahydrodibenz[*c,h*]acridinium salts (**14**) were reduced regiospecifically by sodium borohydride to the corresponding hexahydroacridines (**15**) (Table 1; analytical data are given in Table 5; part of a Supplementary Publication*). In the ^1H n.m.r. spectra (Table 6) of these 1,4-dihydropyridines (**15**), the *N*-substituent α-methylene protons in (**15a—c**) are shifted upfield (to δ 3.3) compared with the corresponding signal (at δ 5.5) for (**14**). The remaining *N*-alkyl substituent protons showed as a multiplet at δ 0.7—1.7. The five ring methylene groups produced a multiplet at δ 1.9—3.2. A muliplet at δ 7.7 was displayed for 1-H and 13-H in (**15a—c**) and the remaining aromatic protons showed as a multiplet at δ 7.0—7.5. The aromatic region in (**15d—f**) by contrast showed only a multiplet at δ 6.5—8.0, for the same reason as discussed above.

Formation of Hydrocarbons from Hexahydroacridines and from Tetrahydroacridinium Salts.—As expected, the hexahydroacridines (**15**) on pyrolysis afforded the corresponding hydrocarbons RH. The temperatures required for these pyrolyses [(140—180 °C for R = alkyl (see Table 1); 250—280 °C for R = aryl)] are not very much lower than those needed for the monocyclic analogues (**8**), and thus this sequence has little synthetic interest. However, we found that a variety of 14-alkyl-5,6,8,9-tetrahydrodibenz[*c,h*]acridinium trifluoromethanesulphonates (**14**) when heated with 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) at 100—140 °C gave the corresponding alkanes in synthetically useful yields (Table 1).

We then turned to the 7-phenyl analogues (**12**), the synthesis of which as trifluoromethanesulphonate salts has already been described.[8,9] These salts, when heated with DBN at 110—140 °C, also gave the n-alkanes in the following yields: n-hexane 60%, n-heptane 65%, n-octane 85%, n-undecane 60%, n-dodecane 60%.

The hydrocarbons were characterised by their ^{13}C spectra (Table 7; treated as part of a Supplementary Publication*) which showed excellent agreement with literature values. Gas chromatography (column 3% OVI on 100—200 mesh Chromosorb WHP at 80 °C with helium as the carrier gas at a flow rate of 20 ml/min) revealed that all the n-alkanes were >99% pure.

We have reported[9] that the *N*-alkyl-7-phenylhydroacridinium salts (**12**) when heated alone give alkenes: when heated with various other bases, (**12**) give mixtures of alkanes and alkenes.[10] The reaction mechanism is probably free radical, with hydrogen abstraction from both the CH_2CH_2 ring of the acridinium and the DBN.[10]

Conclusions.—The successive formation of 14-substituted tetrahydroacridinium salts (**12**) and the heating of these with DBN gives a convenient two-stage deamination of aliphatic amines.

Experimental

Melting points (uncorrected) were determined on a Reichert hot-stage microscope. I.r. spectra were measured for $CHBr_3$ mulls with a Perkin-Elmer 257 instrument. ^1H N.m.r. and ^{13}C n.m.r. spectra were recorded with a Varian EM 360 L and JEOL FX 100 spectrometers, respectively ($SiMe_4$ as an internal standard). Gas chromatographic chromatograms were recorded using a Pye 104 gas chromatograph. The column employed was 3% OV1 on 100—120 mesh Chromosorb WHP at 80 °C with helium as the carrier gas at a flow rate of 20 ml/min.

14-*Alkyl*-5,6,7,8-*tetrahydro*-7-*phenyldibenz*[c,h]*acridinium Trifluoromethanesulphonate* (**12**).—The preparation of these compounds has been reported previously:[9] n-heptyl, m.p. 182—183 °C (lit.,[9] 183 °C); n-octyl, m.p. 146—148 °C (lit.,[9,11] m.p. 147—148 °C); n-undecyl, m.p. 156—157 °C (lit.,[9] m.p. 157—158 °C); n-dodecyl, m.p. 156—157 °C (lit.,[12] m.p. 155—156 °C). The *n-hexyl* derivative m.p. 130 °C was prepared analogously [(Found: C, 68.65; H, 5.9; N, 2.4. $C_{34}H_{34}F_3NO_3S$ requires C, 68.8; H, 5.7; N, 2.35%); δ (60 MHz, $CDCl_3$) 8.4—8.7 (2 H, m), 7.2—7.8 (11 H, m), 5.45 (2 H, t, *J* 5 Hz), 2.85 (8 H, br s), and 0.5—1.5 (11 H, m)].

5,6,8,9-*Tetrahydrodibenzo*[c,h]*xanthylium Trifluoromethanesulphonate* (**13**).—To a mixture of 2-hydroxymethylene-3,4-dihydronaphthalen-1(2*H*)-one[6] (10.44 g, 0.06 mol), 3,4-dihydronaphthalen-1(2*H*)-one (8.8 g, 0.06 mol) and Et_2O (5 ml) was added trifluoromethanesulphonic acid (9.0 g, 0.06 mol). The

* See footnote on page 1671.

mixture was stirred at 25 °C for 45 min, and then stirred with Et_2O (200 ml) to give yellow crystals of the *dibenzoxanthylium trifluoromethanesulphonate* (**13**). They were collected and crystallized from acetone (22 g, 84%), m.p. 210—212 °C (Found: C, 60.6; H, 3.85. $C_{22}H_{17}F_3O_4S$ requires C, 60.84; H, 3.91); $\nu_{max.}$($CHBr_3$) 2 225w, 1 625s, 1 605s, 1 590m, 1 550s, 1 525s, and 1 180—1 260br; δ($CDCl_3$) 3.15 (8 H, s), 7.2—7.8 (6 H, m), 8.0—8.3 (2 H, m), and 8.5 (1 H, s).

General Procedure for 14-*Substituted* 5,6,8,9-*Tetrahydrodibenz*[c,h]*acridinium Trifluoromethanesulphonates* (**14**).—*Procedure A.* To a suspension of (**13**) (2.2 g, 0.005 mol) and triethylamine (0.5 g, 0.005 mol) in sodium-dried ether (50 ml) was added the corresponding alkyl amine (0.005 mol). After the mixture had been stirred for 9 h at 25 °C, the solvent was removed (at 40 °C/0.5 mmHg) to give (**14**) (see Table).

Procedure B. To a suspension of (**13**) (10.0 g, 0.023 mol) in sodium-dried ether (200 ml) was added the corresponding arylamine (0.069 mol). After the mixture had been stirred at 25 °C for 1 h, triethylamine (6.98 g, 0.069 mol) and acetic acid (1.38 g, 0.023 mol) were added and stirring was continued at 25 °C for a further 9 h. The compound separated (Table).

General Procedure for 14-*Substituted* 5,6,7,8,9,14-*Hexahydrodibenz*[c,h]*acridines* (**15**).—Sodium borohydride (0.63 g, 0.016 mol) was added to an ice-cooled solution of the acridinium salt (**14**) (0.016 mol) in Et_2O (50 ml) or acetonitrile–methanol (1:1; 50 ml). The mixture was stirred for 2 h to give the crystalline product (see Table 4).

Thermolysis of 14-*Aryl*-5,6,7,8,9,14-*hexahydrodibenz*[c,h]*acridines.*—The acridine was heated at 250—280 °C and the distillate collected and identified by ^1H n.m.r. and i.r. spectroscopy as benzene (80%) [from (**15d**)]; toluene (90%) [from (**15e**)]; and anisole (90%) [from (**15f**)]. The 14-alkyl derivatives were pyrolysed to give products as described in Table 1.

General Procedure for the Thermolysis of 14-*Substituted* 7-*Phenyl*-(**12**) *and* 14-*Substituted* 5,6,8,9-*Tetrahydrodibenz*[c,h]*acridinium Trifluoromethanesulphonates* (**14**) *with DBN.*—The appropriate salt (0.5—1.0 mmol) and DBN (1 equiv.) were heated at 110 °C/750 mmHg for 1 h, and then at 140 °C/400 mmHg for a further 2 h in a closed apparatus connected to a trap cooled at −45 °C. Details of the products are shown in Tables 1 and 7 (treated as part of the Supplementary Publication *).

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* See footnote on page 1671.

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