Modern Friedel-Crafts chemistry. Part 32.†
Facile synthesis of some new fused heteropolycycles via direct intramolecular Friedel-Crafts cyclialkylations of suitable heteroarylalkanols


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Abstract
This study provides expedient methods for the synthesis of some novel fused heteropolycycles. Thus, a variety of fused di-, tri- and tetracyclic nitrogen and nitrogen-sulfur heteropolycycles 8, 9, 11-15 were smoothly synthesized by Friedel-Crafts intramolecular alkylation of heteroarylalkanols 1-7 in the presence of both Brønsted (PPA and PTSA) and Lewis (AlCl3/CH3NO2) acid catalysts. The precursor alkanols were readily prepared by reaction of the corresponding carboxylic acid esters with methylmagnesium iodide. The structures of the compounds are established using both spectral and analytical data. A plausible carbocation mechanism is proposed to account for the results.

Keywords: Friedel-Crafts cyclialkylation, heteropolycycles, 4,4-dimethyl-5,6-dihydro-4H-pyrido[3,2,1-jk]carbazole, 3,3-dimethyl-2,3-dihydro-1H-benzo[kl]acridine, 5,5-dimethyl-2-phenyl-4,5-dihydrocyclopenta[de]quinoline, 3,3-dimethyl-2,3-dihydro-1H-pyrido[3,2,1-kl]phenothiazine

Introduction
A variety of methods have been developed for the synthesis of biologically and pharmacologically active heteropolycycles that bear quinoline or tetrahydroquinoline fragments.1,2 Among these methods, intramolecular Friedel-Crafts reactions (called cyclialkylation3) prompted by both Brønsted and Lewis acid catalysts proved to introduce powerful pathways for the facile construction of not only homo- but also heteropolycycles.4,5
In this paper, we introduce the construction of seven nitrogen and nitrogen-sulfur polycycles 8, 9, 11-15 containing fused quinoline, tetrahydroquinoline, acridine, phenothiazine and indole moieties via Friedel-Crafts cyclialkylations of seven new heteroarylalkanols 1-7 (Scheme 1).

† For preceding paper of the series see ref 19. Part of the Ph.D. Thesis of H. A. K. Abdel-Aal

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Scheme 1. Selected heteroarylalkanols 1-7.

Results and Discussion

Synthesis and cyclialkylation of 4-(9H-carbazol-9-yl)-2-methylbutan-2-ol (1). This hitherto unknown 4-(9H-carbazol-9-yl)-2-methylbutan-2-ol 1 was synthesized in two consecutive steps starting from 3-(9H-carbazol-9-yl)propanoic acid6 by conversion to ethyl ester followed by reaction with methylmagnesium iodide.

Cyclialkylation of alcohol 1 in the presence of both polyphosphoric acid (PPA) and p-toluenesulfonic acid (PTSA) catalysts gave 4,4-dimethyl-5,6-dihydro-4H-pyrido[3,2,1-jk]carbazole 8 as sole product. The results are presented in Scheme 2 and Table 1 (Entries 1 and 2).

Table 1. Cyclialkylation conditions and results of heteroarylalkanols 1-7

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<tr>
<th>Entry</th>
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<th>Catalyst type</th>
<th>Solvent</th>
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<th>Time hr.</th>
<th>Yield %</th>
<th>Product composition (%)</th>
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<sup>a</sup>With PPA catalyst reactant proportions were: carbinol (0.5 g) and PPA (3 g).  
<sup>b</sup>With PTSA catalyst reactant proportions were: carbinol (0.5 g), PTSA (3 g) and solvent (10 ml).  
<sup>c</sup>With AlCl<sub>3</sub>/CH<sub>3</sub>NO<sub>2</sub> catalyst reactant proportions were: carbinol (0.002 mole), AlCl<sub>3</sub> (0.0024 mole), CH<sub>3</sub>NO<sub>2</sub> (0.024 mole), solvent (10 ml).  
<sup>d</sup>Dichloromethane.  
<sup>e</sup>With H<sub>3</sub>PO<sub>4</sub> catalyst proportions were: carbinol (0.5 g) and dry H<sub>3</sub>PO<sub>4</sub> (4 g).

Synthesis and cyclialkylation of 4-(acridin-9-yl)-2-methylbutan-2-ol (2)
The title alcohol was synthesized by addition of methymagnesium iodide to methyl 3-(acridin-9-yl)propanoate.  
Cyclialkylation of carbinol 2 was carried out using PPA and AlCl<sub>3</sub>/CH<sub>3</sub>NO<sub>2</sub> catalysts in methylene chloride solvent. The product from PPA was shown to be pure 3,3-dimethyl-2,3-dihydro-1H-benzo[kl]acridine 9. With AlCl<sub>3</sub>/CH<sub>3</sub>NO<sub>2</sub> for 2 hours, however, the
The product was shown to be a mixture of tetracyclic product 9 (60%) and 9-(3-methylbut-2-en-1-yl)acridine 10 (35%) (Scheme 3; Table 1, Entries 3 and 4).

**Scheme 3.** Cyclialkylation of 4-(acridin-9-yl)-2-methylbutan-2-ol 2.

**Synthesis and cyclialkylation of 2-methyl-4-(10H-phenothiazin-10-yl)butan-2-ol (3)**

Alkanol 3 was synthesized by treatment of ethyl 3-(10H-phenothiazin-10-yl)propanoate with methylmagnesium iodide in dry ether. Cyclialkylation of 3 in the presence of PPA and PTSA catalysts gave 3,3-dimethyl-2,3-dihydro-1H-pyrido[3,2,1-kl]phenothiazine 11 as a sole product (Scheme 4; Table 1, Entries 5 and 6).

**Scheme 4.** Cyclialkylation of 2-methyl-4-(10H-phenothiazin-10-yl)butan-2-ol 3.

**Synthesis and cyclialkylation of 2-methyl-4-(1,2,3,4-tetrahydro-4H-carbazol-9-yl)butan-2-ol (4)**

This alcohol was obtained in a series of two consecutive steps starting with 3-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)propanoic acid. This acid was converted to its ethyl ester followed by addition of two equivalents of methylmagnesium iodide.

Cyclialkylation of carbinol 4 was carried out in the presence of PPA, H₃PO₄ and PTSA catalysts. The products of reactions with all three catalysts were identical and were shown to be...
4,4-dimethyl-5,6,8,9,10,11-hexahydro-4H-pyrido[3,2,1-jk]carbazole 12 (Scheme 5; Table 1, Entries 7-9).

**Scheme 5.** Cyclialkylation of 2-methyl-4-(1,2,3,4-tetrahydro-4H-carbazol-9-yl)butan-2-ol 4.

**Synthesis and cyclialkylation of 2-methyl-1-(2-phenylquinolin-4-yl)propan-2-ol (5)**

This alcohol was obtained in a series of five consecutive steps starting with (2-phenylquinolin-4-yl)methanol. A summary of the steps and of the involved product intermediates is given in the experimental section. Reaction of carbinol 5 in the presence of PTSA and PPA catalysts gave 5,5-dimethyl-2-phenyl-4,5-dihydrocyclopenta[de]quinoline 13 as a sole product (Scheme 6; Table 1, Entries 10 and 11).

**Scheme 6.** Cyclialkylation of 2-methyl-1-(2-phenylquinolin-4-yl)propan-2-ol 5.

**Synthesis and cyclialkylation of 4-(diphenylamino)-2-methylbutan-2-ol (6)**

This alcohol was obtained by addition of two equivalents of methylmagnesium iodide to ethyl 3-(diphenylamino) propanoate.

The cyclialkylation of alcohol 6 was carried out in the presence of both PPA and PTSA catalysts under different reaction conditions. The products with both catalysts were identical and were shown to be 4,4-dimethyl-1-phenyl-1,2,3,4-tetrahydroquinoline 14 (Scheme 7; Table 1, Entries 12 and 13).

**Scheme 7.** Cyclialkylation of 4-(diphenylamino)-2-methylbutan-2-ol 6.
Synthesis and cyclialkylation of 2-methyl-4-(2-phenyl-1H-indol-1-yl)butan-2-ol (7)

The title alcohol was synthesized via two consecutive reaction steps starting from 3-(2-phenyl-1H-indol-1-yl)propanoic acid\textsuperscript{12} by esterification to ethyl 3-(2-phenyl-1H-indol-1-yl)propanoate followed by reaction with two equivalents of methylmagnesium iodide. Cyclialkylation of alkanol 7 in the presence of either PPA or PTSA catalyst gave 6,6-dimethyl-2-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline 15 as a sole product (Scheme 8; Table 1, Entries 14 and 15).


Conclusions

In conclusion, we have developed a facile and efficient approach to synthesize seven new heteropolycycles 8, 9, 11-15 via intramolecular Friedel-Crafts cyclialkylations of seven new heteroarylalkanols 1-7. All together, the results of this study proved that Friedel-Crafts cyclialkylation can be considered as one of the most useful pathways to the synthesis of di-, tri- and higher condensed polycycles enclosing one or more heteroatoms.

Experimental Section

General. Melting points were measured on a digital Gallenkamp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Shimadzu 470 Infrared spectrophotometer using KBr wafer and thin film techniques (ν cm\textsuperscript{-1}). \textsuperscript{1}H NMR spectra were recorded by 90 MHz Varian NMR spectrometer using the appropriate deuteriated solvent with TMS as internal standard. Chemical shifts (δ) and J values are reported in ppm and Hz, respectively. Elemental analyses were performed on a Perkin-Elmer 2400 Series II analyzer. The mass spectra were performed by JEOL JMS 600 spectrometer at an ionizing potential of 70 eV using the direct inlet system. Reactions were monitored by thin layer chromatography (TLC) using precoated silica plates (Kieselgel 60, F 254, E. Merck) visualized with UV light. Flash column chromatography (FC) was performed on silica gel (230-400 mesh, E. Merck). All reagents were purchased from Merck, Sigma or Aldrich Chemical Co. and were used without further purification.
4-(9H-Carbazol-9-yl)-2-methylbutan-2-ol (1). Was obtained in a series of two consecutive steps starting with 3-(9H-carbazol-9-yl)propanoic acid.\(^6\) A summary of the steps and of the involved product intermediates is given in the following:

(i) Esterification of 3-(9H-carbazol-9-yl)propanoic acid with ethanol as usual\(^1\(^3\) in the presence of pure ethanolic HCl gave the ethyl 3-(9H-carbazol-9-yl)propanoate in the form of pale yellowish oil (79%): mp\(^2\)(25) 157.22; IR (KBr) \(v\) 3050, 2990, 1730, 1620, 1590, 1480, 1455, 1320, 1180, 745 \(\text{cm}^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 0.7\) (3H, t, \(J = 9\) \(\text{Hz}\), CH\(_3\)), 2.4 (2H, t, \(J = 7.5\) \(\text{Hz}\), CH\(_2\)), 3.6 (2H, q, \(J = 9\) \(\text{Hz}\), CH\(_2\)), 4.2 (2H, t, \(J = 7.5\) \(\text{Hz}\), CH\(_2\)) and 6.8-7.1 (8H, m, Ar-H); MS (EI, 70 eV) \(m/z\) (%), 267 (M\(^+\), 22.8), 252 (M\(^+\)-CH\(_3\), 46.3), 239 (15.7), 238 (M\(^+\)-C\(_2\)H\(_5\), 74.5), 222 (100), 208 (9.6), 194 (15.7), 166 (45.6), 91 (8.4), 77 (4.2).

(ii) Addition of two equivalents of methylmagnesium iodide to ethyl 3-(9H-carbazol-9-yl)propanoate was followed by stirring overnight and decomposition by sat. aq. NH\(_4\)Cl soln. Extraction of the product with ether, drying over anhydrous magnesium sulfate, decantation and evaporation of the solvent gave (87%) of the pure product which on crystallization from methanol gave the product in the form of pale brown crystals (93%) of white crystals: mp. 82 \(\degree\)C; IR (KBr) \(v\) 3350, 3250, 3060, 2960, 2850, 1590, 1480, 1460, 1450, 1345, 1145, 915, 740, 670 \(\text{cm}^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.2\) (6H, s, 2CH\(_3\)), 1.6 (1H, s, OH exchangeable with D\(_2\)O), 1.8 (2H, t, \(J = 7.5\) \(\text{Hz}\), CH\(_2\)), 4.3 (2H, t, \(J = 7.5\) \(\text{Hz}\), CH\(_2\)) and 7.1-8.2 (8H, m, Ar-H). Anal. Calcd. for C\(_{17}\)H\(_{19}\)NO (253): C, 80.63; H, 7.5; N, 5.53. Found: C, 80.22; H, 7.61; N, 5.82.

4-(Acridin-9-yl)-2-methylbutan-2-ol (2). Addition of two equivalents of methylmagnesium iodide to methyl 3-(acridin-9-yl)propanoate\(^7\) was followed by stirring overnight. Decomposition by sat. aq. NH\(_4\)Cl soln following standard procedure\(^4\) gave (93%) of crude solid product. Crystallization from methanol gave the product as yellow needles (86%): mp. 110-11 \(\degree\)C; IR (KBr) \(v\) 3350, 3220, 2980, 1610, 1550, 1515, 1480, 1365, 1145, 950, 740, 680 \(\text{cm}^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.2\) (6H, s, 2CH\(_3\)), 1.4 (1H, s, OH exchangeable with D\(_2\)O), 1.7 (2H, apparent m, \(J = 6\) \(\text{Hz}\), CH\(_2\)), 3.6 (2H, apparent m, \(J = 6\) \(\text{Hz}\), CH\(_2\)) and 7.2-8.3 (8H, m, Ar-H). Anal. Calcd. for C\(_{18}\)H\(_{19}\)NO (265): C, 81.5; H, 7.16; N, 5.28. Found: C, 81.77; H, 6.85; N, 5.52.

2-Methyl-4-(10H-phenothiazin-10-yl)butan-2-ol (3). Addition of two equivalents of methylmagnesium iodide to ethyl 3-(10H-phenothiazin-10-yl)propanoate\(^8\) was followed by stirring for 15 hours and decomposition by sat. aq. NH\(_4\)Cl soln. Extraction following the standard procedure\(^4\) gave (78%) of the crude product which on crystallization from methanol gave (70%) of pure 2-methyl-4-(10H-phenothiazin-10-yl)butan-2-ol in the form of pale brown crystals: mp. 70-71 \(\degree\)C; IR (KBr) \(v\) 3280, 3070, 2980, 1590, 1565, 1445, 1370, 1220, 1120, 1030, 720 \(\text{cm}^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.15\) (6H, s, 2CH\(_3\)), 1.7 (2H, d, \(J = 9\) \(\text{Hz}\), CH\(_2\)), 2.3 (1H, s, OH exchangeable with D\(_2\)O), 3.75 (2H, t, \(J = 9\) \(\text{Hz}\), CH\(_2\)) and 6.7-7.3 (8H, m, Ar-H). Anal. Calcd. for C\(_{17}\)H\(_{19}\)NOS (285): C, 71.57; H, 6.66; N, 4.91; S, 11.22. Found: C, 71.92; H, 6.25; N, 5.2; S, 11.31.

2-Methyl-4-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)butan-2-ol (4). Was obtained in two steps starting from 3-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)propanoic acid\(^9\) as follows:
(i) Esterification of the above acid with ethanol and H$_2$SO$_4$ following the literature procedure$^{13}$ gave (91%) of crude solid ester. Crystallization from n-hexane/benzene (7:3) mixture gave (86%) of pure ethyl 3-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)propanoate as pale yellow crystals m.p. 54 °C; IR (KBr) v 3050, 2995, 2910, 1725, 1610, 1463, 1440, 1420, 1375, 1180, 735 cm$^{-1}$; $^1$H NMR (90 MHz, CDCl$_3$, ppm), δ = 1.2 (3H, t, J = 7.5Hz, CH$_3$), 1.8 (4H, d, cyclic 2CH$_2$), 2.7 (6H, m, cyclic 2CH$_2$ and C$_2$H$_2$), 4.2 (2H, q, J = 7.5Hz, CH$_2$), 4.2 (2H, t, J = 7.5Hz, C$_3$H$_2$) and 6.9-7.4 (4H, m, Ar-H); MS (EI, 70 eV) m/z (%), 272 (M$^+$+1, 9.2), 271 (M$^+$, 20.3), 256 (M$^+$–CH$_3$, 31.7), 242 (M$^+$–C$_2$H$_5$, 12.9), 226 (M$^+$–OC$_2$H$_5$, 100), 198 (43.4), 184 (24.3), 170 (39.2), 166 (33.5), 158 (5.3), 91 (4.9), 77 (3.5).

(ii) Addition of two equivalents of methylmagnesium iodide to ethyl 3-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)propanoate followed by stirring for ten hours and decomposition by sat. aq. NH$_4$Cl soln following the standard procedure$^4$ gave (95%) of crude solid product. Crystallization from methanol gave (87%) of 2-methyl-4-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)butan-2-ol 4 in the form of brown crystals: m.p. 68 °C; IR (KBr) v 3380, 3040, 2970, 2910, 1610, 1465, 1438, 1370, 1210, 1210, 1140, 740 cm$^{-1}$; $^1$H NMR (90 MHz, CDCl$_3$, ppm), δ = 1.3 (6H, s, 2CH$_3$), 1.5 (1H, s, OH exchangeable with D$_2$O), 2.6-2.9 (6H, m, cyclic 2CH$_2$ and C$_3$H$_2$), 2.7 (4H, apparent s, unresolved cyclic 2CH$_2$), 4.0-4.3 (2H, t, J = 9Hz, C$_3$H$_2$) and 7.0-7.6 (4H, d, Ar-H). Anal. Calcd. for C$_{17}$H$_{23}$NO (257): C, 79.37; H, 8.94; N, 5.44. Found: C, 79.1; H, 8.57; N, 5.72.

2-Methyl-1-(2-phenylquinolin-4-yl)propan-2-ol (5) was obtained in a series of five consecutive steps starting with (2-phenylquinolin-4-yl)methanol. A summary of the steps and of the involved product intermediates is given in the following:

(i) Following standard literature procedure and reactant ratios,$^{14}$ a solution of thionyl chloride in dry benzene was added dropwise to an ice cooled stirred solution of (2-phenylquinolin-4-yl)methanol in dry benzene over a period of five minutes. The reaction mixture was left to stir for ten more minutes, treated with aqueous ammonia until alkaline then the precipitated hydrochloride was decomposed by water to give (88%) of a crude solid product. Crystallization from petroleum ether (60-80 °C) gave (83%) of pure 4-(chloromethyl)-2-phenylquinoline as white needles: m.p. 112 °C; IR (KBr) v 3070, 2920, 2890, 1595, 1550, 1490, 1350, 1080, 765, 697 cm$^{-1}$; $^1$H NMR (90 MHz, CDCl$_3$, ppm), δ = 4.7 (2H, s, CH$_2$) and 7.4-8.5 (10H, m, Ar-H); MS (EI, 70 eV) m/z (%), 255.6 (M$^+$+2, 7.3), 253.4 (M$^+$, 15.6), 218 (100), 217 (M$^+$–HCl, 45.8), 203 (17.9), 176 (77.6), 166 (18.5), 141 (12.4), 127 (9.8), 90 (14.2), 77 (4.6).

(ii) A solution of 4-(chloromethyl)-2-phenylquinoline in ethanol was added during 30 minutes to a refluxing solution of potassium cyanide in water and ethanol mixture (1:3). After refluxing for four hours, excess alcohol was evaporated and the residue was diluted with water. Extraction of the product with ether, drying over anhydrous magnesium sulfate, decantation and evaporation of the solvent gave (84%) of crude solid product. Crystallization from acetone gave (75%) of pure (2-phenylquinolin-4-yl)acetonitrile in the form of white needles: m.p. 139 °C; IR (KBr) v 3050, 2920, 2350, 1595, 1510, 1410, 1360, 1160, 1085, 785 cm$^{-1}$; $^1$H NMR (90 MHz, CDCl$_3$, ppm), δ = 5.3 (2H, s, CH$_2$) and 7.4-8.5 (10H, m, Ar-H); MS (EI, 70 eV) m/z (%), 244 (M$^+$, 7.2), 217 (M$^+$–HCN, 53.7), 203 (100), 166 (23.5), 140 (13.1), 126 (3.3), 90 (5.2), 77 (3.6).
(iii) Hydrolysis of (2-phenylquinolin-4-yl)acetonitrile to (2-phenylquinolin-4-yl)acetic acid was carried out by refluxing with ethanolic sodium hydroxide solution according to the literature procedure\textsuperscript{13} to give (91\%) of crude solid product. Crystallization from aqueous ethanol gave (81\%) of pure (2-phenylquinolin-4-yl)acetic acid as white needles: m.p. 188-9 °C; IR (KBr) ν 3060, 2900, 2370-2700, 1690, 1595, 1510, 1410, 1215, 785 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), δ = 3.9 (2H, s, CH\(_2\)), 7.2-8.0 ppm (10H, m, Ar-H) and 10.4 (1H, s, COOH); MS (EI, 70 eV) m/z (%), 263 (M\(^+\), 12.5), 246 (100), 218 (43.2), 204 (29.3), 169 (18.5), 166 (23.4), 90 (4.1), 77 (5.2).

(iv) Esterification of the above acid with methanol and H\(_2\)SO\(_4\) following the standard method\textsuperscript{13} gave (83\%) of crude ester. Crystallization from methanol gave (71\%) of pure methyl (2-phenylquinolin-4-yl)acetate: m.p. 93-4 °C; IR (KBr) ν 3055, 2950, 1740, 1595, 1510, 1430, 1260, 1160, 787 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), δ = 3.5 (3H, s, CH\(_3\)), 4 (2H, s, CH\(_2\)) and 7.2-8.2 (10H, m, Ar-H); MS (EI, 70 eV) m/z (%), 278 (M\(^+\)+1, 2.7); 277 (M\(^+\), 16.5), 262 (M\(^+\)-CH\(_3\), 100), 246 (12.4), 234 (M\(^+\)-COCH\(_3\), 100), 204 (39.4), 169 (8.4), 166 (18.2), 127 (5.4), 90 (4.2), 77 (2.4).

(v) Finally alcohol was prepared by addition of two equivalents of methylmagnesium iodide to methyl (2-phenylquinolin-4-yl)acetate in dry ether. The reaction mixture was left to stir overnight at room temperature then treated as usual\textsuperscript{4} to give (87\%) of crude product which on purification by FC (basic alumina, benzene eluent) gave (82\%) of pure 2-methyl-1-(2-phenylquinolin-4-yl)propan-2-ol 5 as a yellowish liquid: \(n_D\textsuperscript{25} 1.6512; IR\) (Film) ν 3590, 3430, 3030, 2985, 1590, 1510, 1460, 1375, 1200, 1140, 1020, 900, 780 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), δ = 1 (6H, s, 2CH\(_3\)), 2.2 (1H, s, OH exchangeable with D\(_2\)O), 3 (2H, s, CH\(_2\)) and 6.9-8.1 (10H, m, Ar-H). Anal. Calcd. for C\(_{19}\)H\(_{19}\)NO (277): C, 82.31; H, 6.86; N, 5.05. Found: C, 81.92; H, 7.26; N, 5.17.

4-(Diphenylamino)-2-methylbutan-2-ol (6). This alcohol was prepared by addition of two equivalents of methylmagnesium iodide to ethyl 3-(diphenylamino)propanoate.\textsuperscript{11} The reaction mixture was left to stir overnight and then decomposed with sat. aq. NH\(_4\)Cl soln and the product was extracted with ether following the literature method\textsuperscript{4} to give (81\%) of the crude oily product. Purification by flash chromatography (FC) of the liquid product [neutral alumina, 8:2, petroleum ether (60-80 °C)/benzene eluent] gave (79\%) of pure 4-(diphenylamino)-2-methylbutan-2-ol 6 in the form of a colorless viscous oil: \(n_D\textsuperscript{25} 1.5426; IR\) (Film) ν 3400, 3060, 2990, 1585, 1480, 1360, 1220, 1055, 1020, 745, 692 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), δ = 1.3 (6H, s, 2CH\(_3\)); 1.7 (2H, t, J = 9Hz, CH\(_2\)), 2.7 (1H, s, OH exchangeable with D\(_2\)O); 3.8 (2H, t, J = 9Hz, CH\(_2\)) and 6.9-7.5 (10H, m, Ar-H). Anal. Calcd. for C\(_{17}\)H\(_{21}\)NO (255): C, 80.0; H, 8.23; N, 5.49. Found: C, 79.7; H, 8.3; N, 5.62.

2-Methyl-4-(2-phenyl-1H-indol-1-yl)butan-2-ol (7). This alcohol was synthesized in two consecutive reaction steps starting from 3-(2-phenyl-1H-indol-1-yl)propanoic acid.\textsuperscript{12} (i) Esterification of this acid by ethyl alcohol following the standard procedure\textsuperscript{13} gave (90\%) of crude oily ester. Purification of the ester by FC (basic alumina, benzene eluent) gave (86\%) of pure ester in the form of yellowish liquid: \(n_D\textsuperscript{25} 1.485; IR\) (Film) ν 3050, 2910, 1700, 1600, 1570,
1540, 1445, 1010, 745, 695 cm⁻¹; ¹H NMR (90 MHz, CDCl₃, ppm), δ = 1.0 (3H, t, J = 6Hz, CH₃), 2.5 (2H, t, J = 7.5Hz, C²H₂), 3.9 (2H, q, J = 6Hz, CH₂), 4.4 (2H, t, J = 7.5Hz, C³H₂), 6.5 (1H, s, CH) and 7.0-7.6 (9H, m, Ar-H); MS (EI, 70 eV) m/z (%), 293 (M⁺, 13.9), 278 (M⁺–CH₃, 21.5), 264 (M⁺–C₂H₅, 15.2), 248 (100), 220 (17.3), 187 (6.4), 166 (11.6), 90 (6.8), 77 (4.4).

(ii) The title alcohol was prepared by addition of two equivalents of methylmagnesium iodide to ethyl 3-(2-phenyl-1H-indol-1-yl)propanoate in dry ether followed by stirring for 20 hours and decomposition by sat. aq. NH₄Cl soln. Separation of the product following literature procedure⁴ gave (84%) of crude solid product. Crystallization from petroleum ether (60-80 °C)/benzene mixture gave (82%) of pure 2-methyl-4-(2-phenyl-1H-indol-1-yl)butan-2-ol 7 in the form of buff plates: m.p. 76-77 °C; IR (KBr) ν 3550, 3480, 3050, 2995, 1700, 1600, 1465, 1445, 1345, 1180, 920, 740, 695 cm⁻¹; ¹H NMR (90 MHz, CDCl₃, ppm), δ = 1.25 (6H, s, 2CH₃), 1.7 (2H, t, J = 9Hz, C³H₂), 4.2 (1H, s, OH exchangeable with D₂O), 4.4 (2H, t, J = 9Hz, C⁴H₂), 6.6 (1H, s, CH) and 7.0-7.7 (9H, m, Ar-H). Anal. Calcd. for C₁₉H₂₁NO (279): C, 81.72; H, 7.52; N, 5.01. Found: C, 81.52; H, 7.74; N, 4.83.

Cyclalkylation procedures

The procedures described earlier for cyclalkylation of arylalkanols with AlCl₃/CH₃NO₂, PPA⁶, p-toluenesulfonic acid⁷ (PTSA) and H₃PO₄ were essentially followed.

4,4-Dimethyl-5,6-dihydro-4H-pyrido[3,2,1-jk]carbazole (8). Greenish plates: m.p. 65 °C; IR (KBr) ν 3050, 2975, 1620, 1580, 1490, 1445, 1340, 1330, 1060, 1025 cm⁻¹; ¹H NMR (90 MHz, CDCl₃, ppm), δ = 1.2 (6H, s, 2CH₃), 1.9 (2H, t, J = 6Hz, CH₂), 4.1 (2H, t, J = 6Hz, CH₂) and 7.0-8.2 (7H, d, Ar-H); MS (EI, 70 eV) m/z (%), 235 (M⁺, 85.8), 219 (M⁺–CH₃ –H, 100), 205 (0.8), 204 (M⁺–2CH₃ –H, 25.1), 191 (5.7), 177 (1.4), 166 (12.5), 151 (1.6), 109 (5.3), 90 (0.3), 77 (0.1), 66 (0.2). Anal. Calcd. for C₁₇H₁₇N (235): C, 86.8; H, 7.23; N, 5.95. Found: C, 86.59; H, 7.05; N, 6.2.

3,3-Dimethyl-2,3-dihydro-1H-benzo[kl]acridine (9). Faint yellow oil: nd²⁵ 1.6344, R₉₂ 0.26 (7.2:2.8, n-hexane/benzene eluent); IR (Film) ν 3050, 2910, 1600, 1540, 1520, 1460, 1340, 742 cm⁻¹; ¹H NMR (90 MHz, CDCl₃, ppm), δ = 1.45 (6H, s, 2CH₃), 2.0 (2H, t, J = 7.5Hz, CH₂), 3.5 (2H, t, J = 7.5Hz, CH₂) and 7.35-8.4 (7H, m, Ar-H); MS (EI, 70 eV) m/z (%), 247 (M⁺*, 20.1), 245 (M⁺–2H, 68.5), 232 (M⁺–CH₃, 3.4), 217 (M⁺–2CH₃, 39.1), 203 (49.1), 191 (100), 189 (9.4), 178 (23.4), 166 (17.7), 151 (9.0), 90 (11.4), 77 (2.5), 66 (2.1). Anal. Calcd. for C₁₈H₁₇N (247): C, 87.44; H, 6.88; N, 5.66. Found: C, 87.2; H, 6.95; N, 5.46.

9-(3-Methylbut-2-en-1-yl)acridine (10). Yellow plates: R₁₉ 0.31 (7.2:2.8, n-hexane/benzene eluent); m.p. 61-62 °C; IR (KBr) ν 3050, 2910, 1460, 755 cm⁻¹; ¹H NMR (90 MHz, CDCl₃, ppm), δ = 1.6 (6H, s, 2CH₃), 2.6 (2H, d, J = 9Hz, CH₂), 5.0 (1H, t, J = 6Hz, CH) and 7.0-8.3 (8H, m, Ar-H); MS (EI, 70 eV) m/z (%), 247 (M⁺, 6.6), 245 (M⁺–2H, 100), 232 (M⁺–CH₃, 9.3), 231 (25.9), 217 (M⁺–2CH₃, 57.3), 205 (18.0), 203 (32.8), 192 (49.5), 177 (6.0), 166 (5.4), 150 (7.4), 91 (2.5), 77 (5.8), 66 (1.3). Anal. Calcd. for C₁₉H₁₇N (247): C, 87.44; H, 6.88; N, 5.66. Found: C, 87.53; H, 6.74; N, 5.52.
3,3-Dimethyl-2,3-dihydro-1H-pyrido[3,2,1-kl]phenothiazine (11). Yellowish viscous oil: \(n_d^{25}\) 1.644; IR (Film) \(v\) 3070, 2985, 1600, 1570, 1460, 1430, 1320, 740 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.25\) (6H, s, 2CH\(_3\)), 1.7 (2H, t, \(J = 6\) Hz, CH\(_2\)), 3.4 (2H, t, \(J = 6\) Hz, CH\(_2\)) and 6.6-7.4 (7H, d, Ar-H); MS (EI, 70 eV) \(m/z\) (%), 267 (M\(^+\), 100), 252 (M\(^+\)-CH\(_3\), 8.2), 251 (M\(^+\)-CH\(_3\)-H, 42.6), 236 (M\(^+\)-2CH\(_3\)-H, 15.5), 223 (16.2), 203 (15.2), 191 (2.6), 177 (2.8), 166 (9.1), 91 (0.5), 77 (2.1), 65 (0.2). Anal. Calcd. for C\(_{17}\)H\(_{17}\)NS (267): C, 76.4; H, 6.36; N, 5.24; S, 11.98. Found: C, 76.21; H, 6.52; N, 5.14; S, 11.7.

4,4-Dimethyl-5,6,8,9,10,11-hexahydro-4H-pyrido[3,2,1-jk]carbazole (12). Yellowish viscous oil: \(n_d^{25}\) 1.6352; IR (Film) \(v\) 3050, 2910, 1610, 1490, 1450, 1320, 740 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.25\) (6H, 2s, 2CH\(_3\)), 1.8 (6H, unresolved m, CH\(_2\) and 2CH\(_2\) of tetrahydrocarbazole ring), 2.6 (4H, broad m, 2CH\(_2\)), 3.8 (2H, t, \(J = 6\) Hz, cyclic NCH\(_2\)) and 6.6-7.3 (3H, m, Ar-H); MS (EI, 70 eV) \(m/z\) (%), 241 (M\(^+\)+2, 4.9), 240 (M\(^+\)-1, 26.5), 239 (M\(^+\), 100), 223 (M\(^+\)-CH\(_3\)-H, 31.8), 209 (M\(^+\)-2CH\(_3\)-H, 12.9), 195 (81.5), 181 (87.7), 166 (38.8), 90 (11.1), 77 (41.6), 66 (2.5). Anal. Calcd. for C\(_{17}\)H\(_{21}\)N (239): C, 85.35; H, 8.78; N, 5.85. Found: C, 85.11; H, 8.72; N, 5.84.

5,5-Dimethyl-2-phenyl-4,5-dihydrocyclopenta[d]quinoline (13). Yellowish viscous oil: \(n_d^{25}\) 1.634; IR (Film) \(v\) 3050, 2900-2980, 1590, 1510, 1450, 1355, 1170, 760 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.7\) (6H, s, 2CH\(_3\)), 4.6 (2H, s, CH\(_2\)) and 7.4-8.3 (9H, d, Ar-H); MS (EI, 70 eV) \(m/z\) (%), 215 (11.5), 201 (65.3), 177 (100), 166 (7.3), 90 (0.1), 77 (1.2), 66 (0.6). Anal. Calcd. for C\(_9\)H\(_{17}\)N (259): C, 88.03; H, 6.56; N, 5.4. Found: C, 87.68; H, 6.54; N, 5.27.

4,4-Dimethyl-1-phenyl-1,2,3,4-tetrahydroquinoline (14). White crystals: m.p. 82 °C from methanol; IR (KBr) \(v\) 3040, 2950, 1590, 1490, 1310, 755, 690 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.3\) (6H, s, 2CH\(_3\)), 1.7 (2H, t, \(J = 6\) Hz, CH\(_2\)), 3.5 (2H, t, \(J = 6\) Hz, CH\(_2\)) and 6.6-7.3 (9H, d, Ar-H); MS (EI, 70 eV) \(m/z\) (%), 237 (M\(^+\), 5.9), 236 (M\(^+\)-H, 39.4), 221 (M\(^+\)-CH\(_3\)-H, 56.9), 207 (M\(^+\)-2CH\(_3\), 3.6), 193 (11.6), 179 (18.2), 168 (100), 166 (34.1), 90 (16.0), 77 (4.9), 65 (5.7). Anal. Calcd. for C\(_9\)H\(_{19}\)N (237): C, 86.07; H, 8.01; N, 5.9. Found: C, 85.85; H, 7.92; N, 6.1.

6,6-Dimethyl-2-phenyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline (15). Reddish viscous oil: \(n_d^{25}\) 1.624; IR (Film) \(v\) 3060, 2970, 1600, 1568, 1480, 1440, 1360, 1070, 740, 695 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\), ppm), \(\delta = 1.25\) (6H, 2s, 2CH\(_3\)), 1.8 (2H, t, \(J = 6\) Hz, CH\(_2\)), 4.1 (2H, t, \(J = 6\) Hz, CH\(_2\)), 6.35 (1H, s, CH) and 6.7-7.5 (8H, m, Ar-H); MS (EI, 70 eV) \(m/z\) (%), 262 (M\(^+\)+1, 22.9), 261 (M\(^+\), 86.8), 246 (M\(^+\)-CH\(_3\), 100), 231 (M\(^+\)-2CH\(_3\), 10.3), 217 (10.9), 192 (84.0), 177 (5.7), 167 (6.4), 166 (7.2), 90 (5.8), 77 (74.2), 66 (1.7). Anal. Calcd. for C\(_9\)H\(_{19}\)N (261): C, 87.35; H, 7.27; N, 5.36. Found: C, 87.57; H, 7.44; N, 5.06.
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