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USE OF THE FISCHER REARRANGEMENT IN CONSTRUCTING 16-R-HEXAHYDRO-BISINDOLO[2,3-*a*:3',2'-*j*]ACRIDINES

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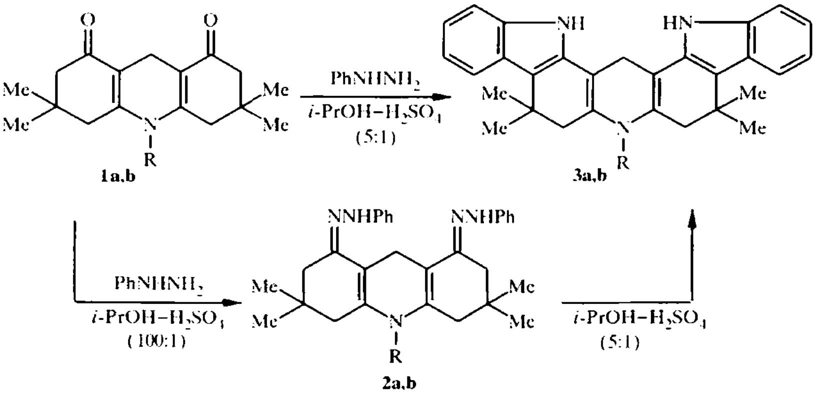
Heating the 3,3,6,6-tetramethyl-1,8-dioxooctrahydroacridine bisphenylhydrazone with P_2O_5 in methanesulfonic acid leads to the product of the Fischer rearrangement, namely, tetrahydrobisindolo[2,3-*a*:3',2'-*j*]-acridine, which contains a central pyridine ring [1].

We have synthesized 6,6,9,9-tetramethyl-N-methyl- and 6,6,9,9-tetramethyl-N-phenyl-6,7,8,9,15,16-hexahydrobisindolo[2,3-*a*:3',2'-*j*]acridines, which are new compounds obtained by the Fischer rearrangement of the bisphenylhydrazones of N-substituted decahydroacridine-1,8-diones **2a,b**. The reaction proceeds without prior separation of the latter in one step upon heating acridinediones **1a,b** with phenylhydrazine in 5:1 2-propanol–concentrated sulfuric acid. The yields of products **3a,b** were 55-59%.



1–3 a R = Me, **b** R = Ph

Under milder conditions using 100:1 2-propanol–concentrated sulfuric acid, the reaction stops upon the formation of bisphenylhydrazones **2a,b** in ~64% yield. These products readily rearrange in 5:1 2-propanol–concentrated sulfuric acid to give hexahydrobisindoloacridines **3a,b** in high yields.

Thus, we are the first to demonstrate the feasibility of using the Fischer reaction for constructing polyazaheterocyclic systems, containing indole and 1,4-dihydropyridine fragments.

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3,3,6,6,9-Pentamethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione Bisphenylhydrazone (2a). A mixture of acridinedione **1a** (10 mmol), phenylhydrazine (30 mmol), 2-propanol (30 ml), and sulfuric acid (0.3 ml) was heated at reflux for 4 h and poured into water (200 ml). The precipitate was filtered off, washed with water (2 × 20 ml), and dried to give compound **2a** in 63% yield; mp 229-231°C (ethanol). IR spectrum: 1550, 1600 (C=C–C=N), 3050 (Ph), 3300 cm^{-1} (NH). ^{1}H NMR spectrum: 8.75 (2H, br. s, NH); 7.45 (4H, m, H_{Ph}); 7.15 (6H, s, H_{Ph}); 3.70 (3H, s, NMe); 3.30 (2H, s, 9,9-H_2); 2.30 (4H, s, CH_2); 2.16 (4H, s, CH_2); 0.97 ppm (12H, s, CMe_2). Found, %: C 77.13; H 7.92; N 15.16. $C_{30}H_{37}N_5$. Calculated, %: C 77.08; H 7.92; N 14.99.

3,3,6,6-Tetramethyl-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione Bisdiphenylhydrazone (2b) was obtained in 64% yield by an analogous procedure from acridinedione **1b**; mp 250-252°C (ethanol). IR spectrum: 1560, 1605 (C=C–C=N); 3050 (Ph); 3320 cm^{-1} (NH). ^{1}H NMR spectrum: 8.82 (2H, br. s, NH); 7.53 (6H, m, H_{Ph}); 7.21 (9H, m, H_{Ph}); 3.25 (2H, s, 9,9-H_2); 2.34 (4H, s, CH_2); 2.12 (4H, s, CH_2); 0.98 ppm (12H, s, CMe_2). Found, %: C 77.76; H 7.45; N 14.55. $C_{35}H_{30}N_5$. Calculated, %: C 77.72; H 7.23; N 14.84.

6,6,9,9,16-Pentamethyl-6,7,8,9,15,16-hexahydrobisindolo[2,3-*a*:3',2'-*j*]acridine (3a). A mixture of acridinedione **1a** (10 mmol), phenylhydrazine (30 mmol), 2-propanol (10 ml), and sulfuric acid (2 ml) was heated at reflux for 6 h and then poured into water (200 ml). The precipitate was filtered off and washed with water (4 × 50 ml) to give compound **3a**. Yield 55%; mp >350°C (ethanol). IR spectrum: 1600 (C=C); 3060 (Ph); 3250 cm^{-1} (NH). ^{1}H NMR spectrum: 9.88 (1H, s, NH); 9.74 (1H, s, NH); 7.38 (4H, m, H_{Ph}); 7.30 (2H, m, H_{Ph}); 7.30 (2H, m, H_{Ph}); 6.88 (2H, m, H_{Ph}); 4.07 (3H, s, NMe); 3.20 (2H, s, 15,15-H_2); 2.63 (4H, s, CH_2); 1.18 (6H, s, CMe_2); 1.12 ppm (6H, s, Me_2). Found, %: C 83.47; H 7.22; N 9.83. $C_{30}H_{31}N_3$. Calculated, %: C 83.14; H 7.16; N 9.70.

6,6,9,9-Tetramethyl-16-phenyl-6,7,8,9,15,16-hexahydrobisindolo[2,3-*a*:3',2'-*j*]acridine (3b) was obtained in 59% yield by an analogous procedure using acridinedione **1b**; mp >350°C (ethanol). IR spectrum: 1600 (C=C); 3070 (Ph); 3260 cm^{-1} (NH). ^{1}H NMR spectrum: 9.90 (1H, s, NH); 9.71 (1H, s, NH); 7.36 (5H, m, H_{Ph}); 7.28 (6H, m, H_{Ph}); 6.86 (2H, m, H_{Ph}); 3.20 (2H, s, 15,15-H_2); 2.65 (4H, s, CH_2); 1.16 (6H, s, CMe_2); 1.08 ppm (6H, s, CMe_2). Found, %: C 85.02; H 6.74; N 8.40. $C_{35}H_{33}N_3$. Calculated, %: C 84.85; H 6.67; N 8.48.

Indolo[2,3-*a*:3',2'-*j*]acridines **3a,b** were also obtained from compounds **2a,b** in 90 and 92% yield, respectively.

REFERENCES

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