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REACTION OF 3,3,6,6-TETRAMETHYL-1,2,3,4,5,6,7,8,9,10-DECAHYDROACRIDINE-1,8-DIONES WITH LITHIUM ALUMINUM HYDRIDE

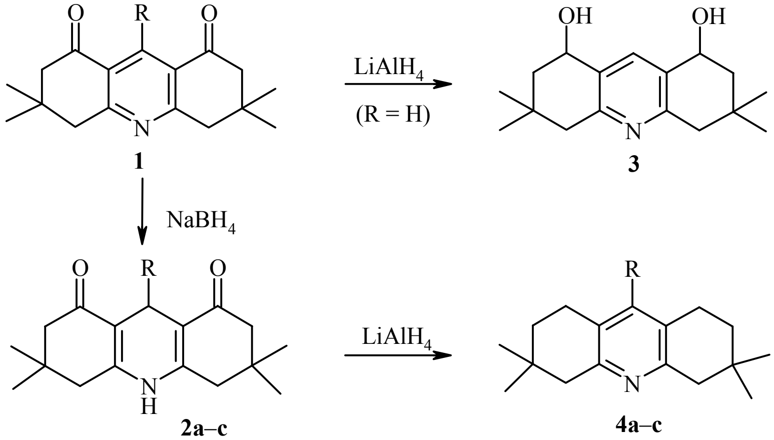
A. N. Pyrko

The corresponding 3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroacridines have been obtained by the interaction of 3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione, its 9-Ph- and 9-p-MeOC$_6$H$_4$-substituted derivatives with lithium aluminum hydride. The reaction proceeds in boiling diglyme and also at room temperature on extended stirring of the reactants in ether.

Keywords: decahydroacridine, reduction with lithium aluminum hydride.

The interaction of 3,5-diacylpyridines with complex metal hydrides (NaBH$_4$, LiAlH$_4$) proceeds with the reduction of either the carbonyl functions to alcohols, or of the pyridine ring to a 1,4-dihydropyridine [1]. In particular the reaction of octahydroacridinedione **1** (R = H) with NaBH$_4$ proceeds with the reduction of the pyridine ring and leads to decahydroacridine **2a** [2], but its interaction with LiAlH$_4$ leads to an octahydroacridinediol **3** [3].

In a series of these compounds it seemed of interest to effect the reduction of the carbonyl functions of decahydroacridinediones **2a-c** with lithium aluminum hydride. It turned out that the reaction proceeds in boiling diglyme and leads to octahydroacridines **4a-c**. In addition the reaction may be also effected at room temperature as was shown by us using the conversion of decahydroacridinedione **2b** to octahydroacridine **4b** as an example. The reduction occurs on extended stirring of the components in ether.



1, **2**, **4** **a** R = H, **b** R = Ph, **c** R = *p*-MeOC$_6$H$_4$

Institute of Bioorganic Chemistry, National Academy of Sciences of Belarus, Minsk 220141; e-mail: labst@iboch.bas-net.by. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1181-1183, August, 2003. Original article submitted August 7, 2000.

TABLE 1. Spectral Characteristics of the Synthesized Compounds **4a-c**

Compound	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	^{1}H and ^{13}C NMR spectra, δ, ppm (*J*, Hz)*
4a	1435, 1460, 1578, 1610, 2930, 2875	210 (3.63), 281 (3.64)	0.98 (12H, s, CH$_3$); 1.54 (4H, t, *J* = 7.0, 2- and 7-CH$_2$); 2.62 (4H, s, 4- and 5-CH$_2$); 2.73 (4H, t, *J* = 7.0, 1- and 8-CH$_2$); 7.10 (1H, s, 9-H) [25.78 (C$_{(2)}$, C$_{(7)}$); 28.72 (CH$_3$); 30.63 (C$_{(3)}$, C$_{(6)}$); 36.01 (C$_{(1)}$, C$_{(8)}$); 46.58 (C$_{(4)}$, C$_{(5)}$); 128.20 (C$_{(8a)}$, C$_{(9a)}$); 137.48 (C$_{(9)}$); 154.32 (C$_{(4a)}$, C$_{(10a)}$)]
4b	1440, 1470, 1555, 1572, 2872, 2920	282 (3.71)	0.99 (12H, s, CH$_3$); 1.44 (4H, t, *J* = 7.0, 2- and 7-CH$_2$); 2.38 (4H, t, *J* = 7.0, 1-, 8-H$_2$); 2.74 (4H, s, 4- and 5-CH$_2$); 7.08 (2H, d, *J* = 7.0, 8'- and 5'-H); 7.41 (3H, m, 2'-, 4'- and 6'-H) [24.40 (C$_{(2)}$, C$_{(7)}$); 28.07 (CH$_3$); 29.87 (C$_{(3)}$, C$_{(6)}$); 35.56 (C$_{(1)}$, C$_{(8)}$); 46.68 (C$_{(5)}$, C$_{(4)}$); 125.70 (C$_{(8a)}$, C$_{(9a)}$); 127.15 (C$_{(2')}$, C$_{(6')}$); 127.85 (C$_{(4')}$); 128.71 (C$_{(3')}$, C$_{(5')}$); 138.71 (C$_{(1')}$); 149.16 (C$_{(9)}$); 153.76 (C$_{(4a)}$, C$_{(10a)}$)]
4c	1445, 1520, 1580, 1620, 2875, 2950	222 (4.08), 282 (3.77)	0.98 (12H, s, CH$_3$); 1.46 (4H, t, *J* = 7.0, 2- and 7-CH$_2$); 2.35 (4H, t, *J* = 7.0, 1- and 8-CH$_2$); 2.72 (4H, s, 4- and 5-CH$_2$); 3.88 (3H, s, OCH$_3$); 6.78 (2H, d, *J* = 8.0, 2'- and 6'-H); 6.90 (2H, d, *J* = 8.0, 3'- and 5'-H) [24.46 (C$_{(2)}$, C$_{(7)}$); 28.02 (CH$_3$); 29.62 (C$_{(3)}$, C$_{(6)}$); 35.56 (C$_{(1)}$, C$_{(8)}$); 46.08 (C$_{(4)}$, C$_{(5)}$); 55.20 (OCH$_3$); 114.16 (C$_{(3')}$, C$_{(5')}$); 126.58 (C$_{(8a)}$, C$_{(9a)}$); 128.95 (C$_{(2')}$, C$_{(6')}$); 130.62 (C$_{(1')}$); 149.47 (C$_{(9)}$); 153.56 (C$_{(4a)}$, C$_{(10a)}$); 158.71 (C$_{(4')}$)]

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* The ^{13}C NMR spectra are given in square brackets.

The structures of compounds **4a-c** were confirmed by spectral data and the results of elemental analysis (Table 1). In the ^{1}H NMR spectra there was a singlet signal for the protons of the four methyl groups at 0.98, 0.99, and 0.98 ppm, a triplet signal for the methylene protons in positions 2 and 7 (1.54, 1.44, and 1.46 ppm) and the methylene protons interacting with them in positions 1 and 8 (2.73, 2.38, and 2.36 ppm), and also a singlet signal for the methylene protons at positions 4 and 5 (2.62, 2.74, and 2.72 ppm). In the ^{13}C NMR spectrum it was possible to assign all the signals unequivocally (Table 1).

It should be noted that the conversion described is an efficient method of transition from the Hantzsch synthesis products to pyridine derivatives containing no oxygen functions.

EXPERIMENTAL

A check on the synthesis and on the homogeneity of the compounds obtained was effected by TLC on Silufol UV 254 plates, eluent ether–hexane, 1:2. Visualization was with UV light or iodine vapor. Melting points were determined on a Boetius stage. The IR spectra were recorded on a UR-20 instrument in KBr disks. The UV spectra were taken on a Specord M-400 spectrometer for solutions in ethanol. The ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ on a Bruker AC-200 instrument (200 and 50 MHz respectively). The ^{13}C NMR spectra were obtained with decoupling from protons.

Decahydroacridinediones 2a-c were obtained by the procedures of [2,4,5].

3,3,6,6-Tetramethyl-9-phenyl-1,2,3,4,5,6,7,8-octahydroacridine (4b). A. Decahydroacridinedione **2b** (698 mg, 2 mmol) in anhydrous diglyme (10 ml) was boiled with lithium aluminum hydride (300 mg, 7.9 mmol) for 1.5 h. After cooling water (2 ml) and ethanol (50 ml) were added carefully to the reaction mixture. The solid was filtered off, the filtrate evaporated, the residue was treated with water (20 ml), ether (200 ml), and the ether solution dried over $MgSO_4$. After evaporation of the ether and crystallization of the residue from ether–hexane, 1:1, hydroacridine **4b** (510 mg: 80%) was obtained; mp 178-180°C (ether–hexane). Found, %: C 86.61; H 9.18; N 4.50. $C_{23}H_{29}N$. Calculated, %: C 86.52; H 9.09; N 4.39.

3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydroacridine (4a) was obtained analogously with a yield of 330 mg (68%) from decahydroacridinedione **2a** (546 mg, 2 mmol); mp 96-98°C (ether–hexane). Found, %: C 83.76; 10.17; 5.88. $C_{17}H_{25}N$. Calculated, %: C 83.95; H 10.29; N 5.76.

9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroacridine (4c) was obtained with a yield of 565 mg (81%) from decahydroacridinedione **2c** (758 mg, 2 mmol); mp 230-235°C (decomp., ethyl acetate–hexane). Found, %: C 82.36; H 8.94; N 4.12. $C_{24}H_{31}N$. Calculated, %: C 82.52; H 8.88; N 4.01.

A. Decahydroacridinedione **2b** (698 mg, 2 mmol) in dry ether (200 ml) was stirred with lithium aluminum hydride (300 mg, 7.9 mmol) at room temperature for 15 h. Water (0.5 ml) was then carefully added and stirring continued for a further 5 h. Water (5 ml) was added carefully and the reaction mixture filtered through a layer (2 cm) of dry Na_2SO_4. After evaporation and crystallization of the residue from ether–hexane, 1:1 the hydroacridine **4b** (490 mg, 77%) was obtained.

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