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CYCLOCONDENSATION AND AROMATIZATION DURING REACTION OF DIMEDONE, *p*-DIMETHYLAMINOBENZALDEHYDE, AND AMMONIUM ACETATE

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Information about products of three-component cyclocondensation of dimedone **1**, *p*-dimethylaminobenzaldehyde **2**, and ammonium acetate **3** is contradictory. According to [1], when boiled in acetic acid they form the decahydroacridine derivative **4**, and "in some cases" a colorless substance which is assigned the structure of octahydroacridine **5**. Formation of the second product is explained by the fact that compound **4** "is easily oxidized by oxygen in the air or disproportionates". However, according to data in [2], compound **4** is stable in DMSO at 120°C for 6 h. It was synthesized under these conditions, and no aromatization products are mentioned (Scheme 1).

We have acquired new facts pertaining to reaction of reagents **1-3**. When they are boiled in ethanol, the formation of compound **4** proceeds selectively. The yield is 90% (according to the method in [1,2], the yield is respectively 56% and 51%). When they are boiled in acetic acid, the reaction does not stop at the stage of formation of product **4**, but also does not lead to compound **5**. Subsequent aromatization, as we have established, occurs with cleavage of N,N-dimethylaniline (detected by TLC) and results in the derivative of octahydroacridine **6** in 85% yield. The latter is obtained more rapidly and in purer form when compound **4** is boiled in acetic acid. The same product is obtained [1] by oxidation of decahydroacridine **7** by nitrous acid, and we have duplicated this synthesis. Samples obtained by the three methods are identical according to TLC data, and mixed samples do not result in depression of the melting point. The structure of compound **6**, and in particular the absence of a *p*-dimethylaminophenyl moiety in it, is confirmed by physical and chemical studies.

Thus the condensation products of aldehyde **2** tend toward cleavage of N,N-dimethylaniline. The phenomenon we observed probably can be used in practical organic synthesis. Favorable factors for this include the accessibility, stability during storage, safety, and easy measurement of quantities of the reagent **2** used. The example we have proposed can be considered as a novel approach to Hansch type synthesis of pyridines, making it possible to construct a γ-unsubstituted pyridine ring, without using an oxidizing agent, according to a simple and very effective procedure.

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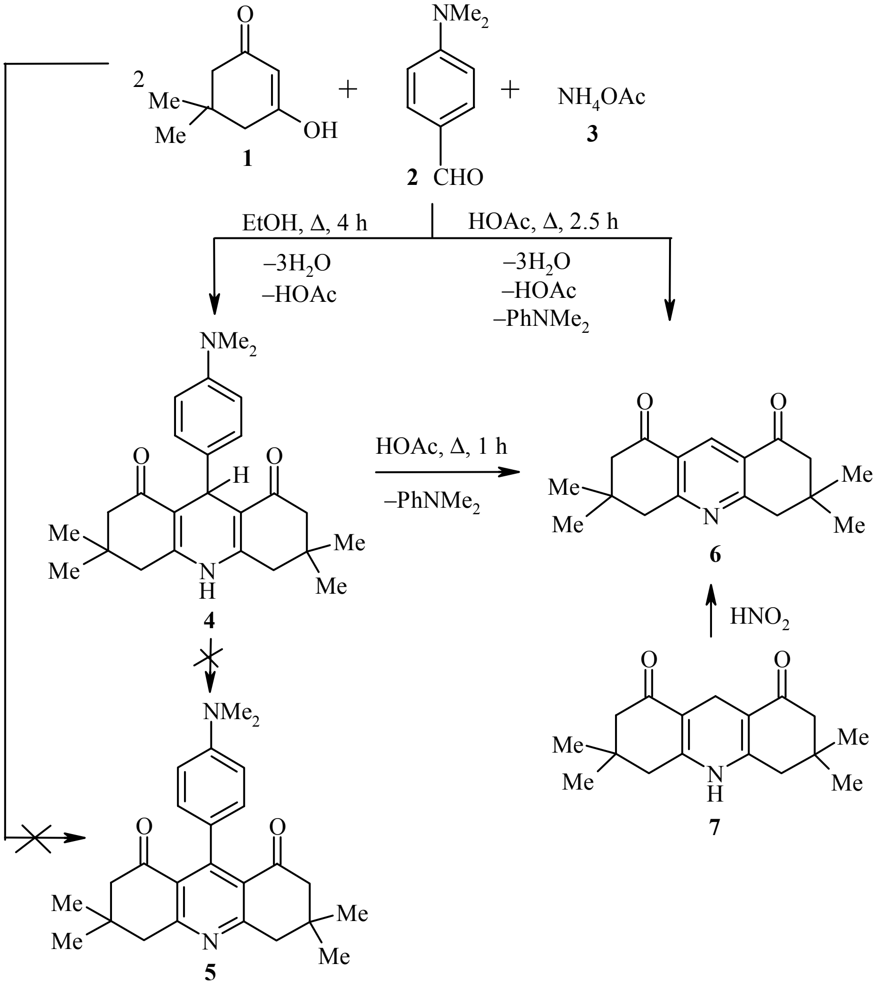
Scheme 1



9-(*p*-Dimethylaminophenyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (4). Compounds **1** (1.4 g, 10 mmol), **2** (0.82 g, 5.5 mmol), and **3** (0.77 g, 10 mmol) in ethanol (7.5 ml) were held for 4 h at 85-90°C. Upon cooling, the precipitate was filtered off and washed with ethanol. Yield 1.76 g (90%), yellow crystals; mp 311-313°C (lit., 293-294°C [1], 311-313°C [2]). The IR spectrum and ^{1}H NMR spectrum match the data in [2].

3,3,6,6-Tetramethyl-1,2,3,4,5,6,7,8-octahydroacridine-1,8-dione (6). A. Compounds **1** (0.56 g, 4 mmol), **2** (0.33 g, 2.2 mmol), and **3** (0.31 g, 4 mmol) in glacial acetic acid (4 ml) were boiled for 2.5 h. The boiling solution was diluted with water (8 ml). On cooling, the precipitate was filtered off and washed with 1:1 aqueous ethanol. Yield, 0.46 g (85%), colorless crystals; mp 150-151°C (lit., 147-148, 146°C [1]). IR spectrum, (KBr), ν, cm^{-1}: 2980, 2890, 1700, 1595. ^{1}H NMR spectrum (300 MHz, DMSO-d$_6$, TMS), ppm: 1.04 (12H, s, 4CH$_3$); 2.59 (4H, s, 2CH$_2$); 3.05 (4H, s, 2CH$_2$); 8.47 (1H, s, CH). ^{13}C NMR spectrum (75.5 MHz, DMSO-d$_6$, TMS): 27.68 (CH$_3$); 39.50 (4- and 5-C); 45.72 (3- and 6-C); 50.98 (2- and 7-C); 125.45 (2C=C–C=O); 131.34 (9-C); 166.31 (2C=N); 196.69 (1- and 8-C). Found, %: C 75.21; H 7.85; N 5.22. $C_{17}H_{21}NO_2$. Calculated, %: C 75.24; H 7.80; N 5.16.

B. Compound **4** (0.78 g, 2 mmol) in glacial acetic acid (4 ml) was boiled for 1 h. The product was isolated similarly to method A. Yield 0.46 g (85%), colorless crystals; mp 150-151°C.

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