Condensation of 1,3-Diketones with 1,8-Diaminonaphthalene: Synthesis of Bis(2,3-dihydroperimidine-2-spiro)cycloalkanes

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Summary. Cyclic 1,3-diketones like cyclopentane-1,3-dione, cyclohexane-1,3-dione, and 5,5-di-methylcyclohexane-1,3-dione react with 1,8-diaminonaphthalene to afford new condensed heterocyclic spiro systems.

Keywords. 1,3-Diketones; 1,8-Diaminonaphthalene; 2,3-Dihydroperimidine; Spiro compounds.

Introduction
The synthesis of perimidine based heterocyclic systems by reaction of 1,8-diaminonaphthalene (1) and carbonyl compounds, [1-3] is of considerable importance in view of their utility as dye intermediates and coloring materials for polymers [4]. In addition, they have been reported to possess anti-inflammatory, CNS depressant, anti-bacterial, and anti-fungal activities [5].

Direct heating of 1 and benzyl methyl ketone results in the formation of toluene and 2-methylperimidine (2, [6]). This observation suggests that similar formation of perimidine derivatives should occur from 1,3-diketones such as pentane-2,4-dione (3). The formation of 2 and 2,2-dimethyl-2,3-dihydroperimidine (4) by heating of 1 with 3 prompted us to examine this reaction using cyclic 1,3-diketones such as 5a, 5b, and 5c. We report here a one-pot synthesis of the hitherto unknown bis(2,3-dihydroperimidine-2-spiro)cycloalkanes 6a, 6b, and 6c.
Results and Discussion

Cyclopentane-1,3-dione (5a) and cyclohexane-1,3-dione (5b) undergo a smooth condensation reaction with 1,8-naphthalenediamine at room temperature to yield the symmetrical 1:2 (diketone:diamine) adducts 6a and 6b, respectively. However, 5,5-dimethylcyclohexane-1,3-dione (6c) afforded, in addition to the expected symmetrical condensation product 6c, a second 1:2 adduct (7) in which the 1,3-dione is incorporated as an acyclic C₆ unit, obviously derived from a retro-Dieckmann type ring cleavage of 5c [7, 8].

The structures of compounds 6a–c and 7 were deduced from their elemental analyses and their IR, ¹H NMR, and ¹³C NMR spectra. The nature of these compounds as 1:2 adducts was apparent from the mass spectra which displayed molecular ion peaks at m/z = 378, 392, and 420. The base peak in the mass spectra of compounds 6a–c and 7 is located at m/z = 182 (C₁₂H₁₀N₂) and corresponds to the 2-methylperimidine ion. The mass spectra of 6c and 7 are similar except for the relative intensities of some peaks. Initial fragmentations involve loss of the 2-methylperimidine moiety.

The ¹H and ¹³C NMR data for compounds 6a–c and 7 are shown in Table 1. The ¹H and ¹³C NMR data for perimidine derivatives 2 and 4 are also given for comparison. The ¹H and ¹³C NMR data for 2-methylperimidine are in agreement with time-averaged C₂ᵥ symmetry which results from a fast 1,3-proton shift [9]. The ¹H NMR spectrum of 6a exhibits signals for methylene protons at 2.11 and