In the series of heterocyclizations of unsaturated carbonyl compounds, cyclocondensations based on ortho-diamines (or more specifically 1,2-diamines) are of particular significance. These reactions are characterized by the formation of different heterocycles with various (sometimes unexpected) structures.

First of all, it should be noted that the products of the “normal” interaction of unsaturated ketones with 1,2-diamines, i.e., dihydrated diazepine and triazepine systems, possess considerable chemical lability and are able to undergo further transformations (multistage, as a rule). Moreover, if there exists an alternative, then the process of seven-membered heterocycle formation is noticeably less advantageous thermodynamically as opposed to that of six- or five-membered structures, especially heteroaromatic ones. Owing to this, the interaction of ortho-diamines with chalcones is characterized either by superimposition of numerous secondary chemical transformations during condensation or by alternative reaction pathways. This has given rise to prolonged discussions concerning the structures of the products formed: in some papers three or more structures based on corresponding spectral and chemical data have been accredited to certain products.

In the present chapter, an attempt is made to systemize the literature data and to analyze the rules of the reactions of 1,2-diamines, both the aromatic and the heteroaromatic nature, with chalcones for the synthesis of specific heterocycles.

### 4.1 Synthesis of 1,5-Dihydroazepines

The interaction of ortho-phenylenediamine (o-PDA) with aliphatic α,β-unsaturated ketones, in particular, mesityl oxide, was reported for the first time as long ago as 1905 [1]. Nevertheless, only in the 1950s was the reaction product convincingly proved to have the structure of dihydrobenzodiazepine [2, 3]. Meanwhile, the condensation reactions of aromatic unsaturated ketones with aromatic and heterocyclic ortho-diamines remained unstudied for a long time. One of the reasons for this situation was attributed to the impossibility of the formation of a dihydrobenzodiazepine cycle by the interaction between o-PDA 1 and chalcone...
[2, 4]. According to the data obtained, such a reaction either does not proceed at all [4] or yields the corresponding β-amino adduct 2 or 2-phenylbenzimiazole 4 [2], depending on the reaction conditions. These results were treated as a general feature of the interaction between o-PDA and chalcones [2]. The impossibility of the formation of aromatic dihydrobenzodiazepine derivatives was explained by the essentially lower reactivity of the carbonyl group in chalcone molecules in comparison with that of the C = C bond.

The first reliable report on the synthesis of 2,4-diphenyl-2,3-dihydro-1H-1,5-benzodiazepine 3 for the reaction of o-PDA and chalcone was published in 1975 [5].

A more detailed study [6] showed the β-amination of an unsaturated ketone and the formation of adduct 2 (Scheme 4.1) to be the first stage of this reaction. Later the general character of the interaction between o-PDA and substituted ketones or their vinylogs was established [7, 8]. Unsuccessful attempts [7] to synthesize aromatic dihydrobenzodiazepine derivatives from 1,2-diaminoanthraquinone, 4-nitro-, 4-nitrile-4,6-dichlor- and N-phenyl-substituted o-PDAs were also reported. Condensation of o-PDA with o-xydroxychalcone 5 (Scheme 4.2) does not produce diazepine derivatives, but 2-(2-oxyphenyl)benzimidazole 6 was found to be the only product isolated. However, there are known data on the interaction between o-PDA and ortho-oxybenzalacetone 7 (the structure of which is similar to that of ortho-oxychalcone) resulting in the formation of benzodiazepine 8 [9]. The reaction involves an intramolecular cyclization in which the hydroxyl group and the azomethine bond participate.