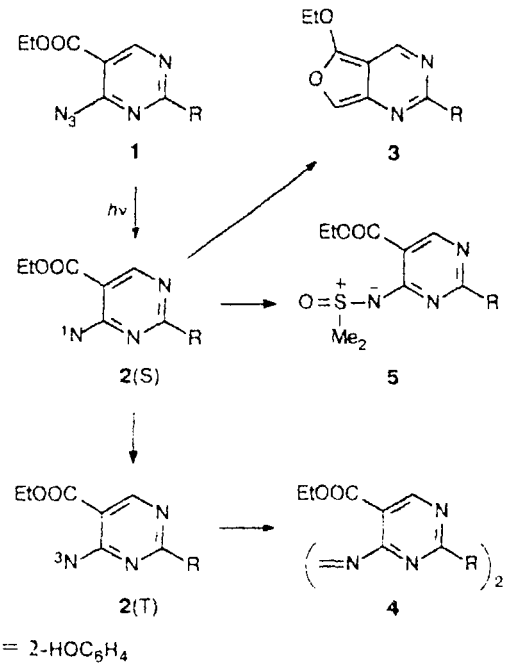
Scheme 1



group.[3] Recently[4] we prepared 3-ethoxy-6-(2-hydroxyphenyl)isoxazolo[3,4-*d*]pyrimidine (**3**) by thermolysis of 4-azido-5-ethoxycarbonyl-2-(2-hydroxyphenyl)pyrimidine (**1**) (Scheme 1). To carry out the photochemical synthesis of **3**, we used the same initial compound, since we assumed that the presence of the N(3) atom in the molecule of **1** would prevent the ring expansion in the intermediate nitrene **2**(S) and would thus be favorable for the competing reaction, *viz.*, intramolecular interaction of nitrene with the ethoxycarbonyl group.

Azide **1** in C_6D_6 was irradiated at 20 °C with filtered UV light in a NMR tube (Wilmad Glass) using a DRSh-500 Hg-lamp and UFS-6 and BS-12 light filters; ^{1}H NMR spectra were recorded at intervals during the process. This allowed us to detect the formation of compound **3**, whose accumulation was accompanied by accumulation of the product of the transformation of triplet nitrene **2**(T), *viz.*, azo-compound **4**.[4] After 1.5 h, the proportions of **3** and **4** were 57% and 43%, respectively, and the degree of conversion of azide **1** was ~80%. Compound **3** is stable under the photolysis conditions. It was also found that during the photolysis of azide **1** in DMSO (2 h), singlet nitrene **2**(S) is trapped by the sulfur atom of the solvent to give *S,N*-ylide **5** in a virtually quantitative yield. This compound is also formed selectively when the solution is irradiated with sunlight.

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A modified synthesis of ellipticine

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Previously,[1] an efficient scheme of synthesis of the known antitumor alkaloid ellipticine (**1**)[2,3] was developed. It is based on a new approach to preparation of the key synthone 1,4-dimethylcarbazole (**2**), which uses a variant of the aromatic amino-Claizen rearrangement we developed. The synthesis of compound **2** involves a series of subsequent processes: *N*-alkenylation, amino-rearrangement, and intramolecular cyclization with iso-

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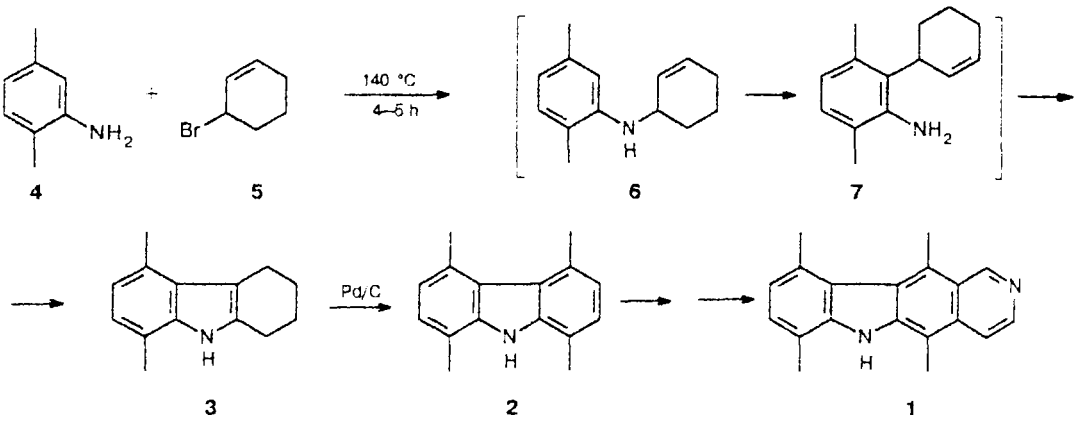

4 5 6 7 3 2 1

lation of the corresponding intermediates. We substantially modified this scheme, which allowed us to obtain 1,4-dimethyltetrahydrocarbazole (**3**) in one technological stage. The reaction of equimolar amounts of 2,5-xylidine (**4**) and 3-bromocyclohexene (**5**) in nitrobenzene at 140 °C for 4—5 h results in the formation of tetrahydrocarbazole **3** in 61% yield. It is established that the amine **6** that formed readily undergoes the Claizen rearrangement, followed by cyclization of *ortho*-alkenylamine **7** to compound **3**. The dehydrogenation of the latter in the presence of Pd/C in trimethylbenzene[4] gives carbazole **2** in 87% yield. The subsequent synthesis was performed by a known procedure.[5] The resulting physicochemical of ellipticine obtained correspond to the published data.[2,5]

The reaction of formation of tetrahydrocarbazole compounds is rather general and was shown to proceed in the case of several arylamines used as examples.

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Unexpected reaction of 6-nitroindolizine with dimethyl acetylenedicarboxylate

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It is known that indolizines readily enter into the so-called [8+2]-cycloaddition reactions allowed by orbital symmetry rules[1—4] to form cycl[3.2.2]azine derivatives. For many years, the reaction mechanism remained under discussion, and the effect of substituents in the pyridine fragment of indolizine on the specific features of this reaction has not yet been studied.

For the first time, we have studied the reaction of 6-nitroindolizine **1** with dimethyl acetylenedicarboxylate (DMAD).

The reaction is completed in 3 h to form cyclazine **4**, which lacks the nitro group, along with the expected nitrocyclazine (**3**) (ratio **3** : **4** 2 : 7). The structures of the compounds obtained were confirmed by their

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