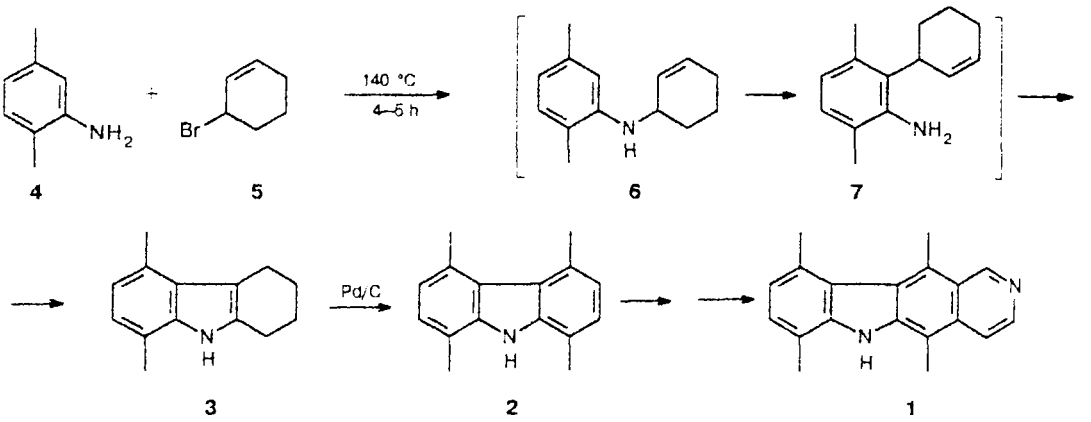

4 5 6 7 3 2 1

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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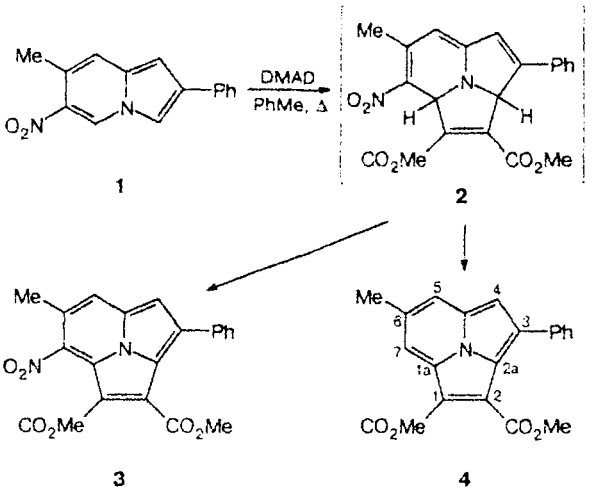

^{1}H NMR and mass spectra, and their elemental analysis data. The ^{1}H NMR spectrum of compound **3** contains singlets of H(4) and H(5) that do not overlap the signals of the protons of the phenyl group. The ^{1}H NMR spectrum of cyclazine **4** contains, along with the same signals, the singlet of the H(7) proton in the lowest field (at 8.14 ppm). The downfield shift of the signal of H(7) to 8.3 ppm was previously reported for 1,2-dimethoxycarbonylcyclazine.[5]

The formation of cyclazine **3** due to dehydrogenation of the adduct of [8+2]-cycloaddition (**2**) is quite similar to the earlier results. Meanwhile, the unexpected elimination of the nitro group during the reaction can be likely attributed to the possible migration of a proton from position 2a to position 7 of the dienamine structure of intermediate **2** followed by elimination of HNO_2.

7-Methyl-6-nitro-2-phenylindolizine (**1**) was obtained by a described procedure.[6] The reaction of nitroindolizine **1** (1.00 g, 3.96 mmol) with dimethyl acetylenedicarboxylate (0.56 mL, 4.55 mmol) in toluene (25 mL) was performed in an atmosphere of argon. The reaction mixture was heated at 100 °C for 3 h. Then the solvent was evaporated *in vacuo*, and the residue was chromatographed on a column with SiO_2 (10 → 33% ethylacetate in hexane). 1,2-Dimethoxycarbonyl-6-methyl-3-phenylcycl[3.2.2]azine (**4**) was isolated in 31% yield (0.424 g). M.p. 185—186 °C. ^{1}H NMR ($CDCl_3$), δ: 2.73 (s, 3 H, Me), 3.94 (s, 3 H, MeOOC), 4.00 (s, 3 H, MeOOC), 7.31 (s, 1 H, H(4)), 7.33—7.55 (m, 3 H, Ph), 7.67 (s, 1 H, H(5)), 7.71—7.81 (m, 2 H, Ph), 8.14 (s, 1 H, H(7)). MS (*m/z*): 347 (M^+). Calculated (%): C, 72.61; H, 4.93; N, 4.03. $C_{21}H_{17}NO_4$. Found (%): C, 72.75; H, 4.83; N, 3.88.

The subsequent fractions gave 1,2-dimethoxycarbonyl-6-methyl-7-nitro-3-phenylcycl[3.2.2]azine **3** (0.133 g, 9%). M.p. 207—209 °C. ^{1}H NMR ($CDCl_3$), δ: 2.72 (s, 3 H, Me), 3.91 (s, 3 H, MeOOC), 3.95 (s, 3 H, MeOOC), 7.40 (s, 1 H, H(4)), 7.42—7.57 (m, 3 H, Ph), 7.68—7.78 (m, 2 H, Ph), 7.80 (s, 1 H, H(5)). MS (*m/z*): 392 (M^+). Calculated (%): N, 7.14. $C_{21}H_{16}N_2O_6$. Found (%): N, 7.00.

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