Letters to the Editor

New *one pot* synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes*

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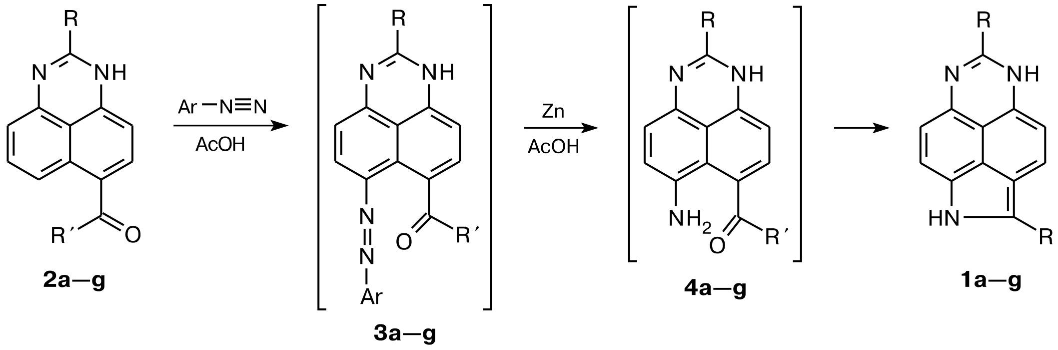
1*H*-1,5,7-Triazacyclopenta[*c,d*]phenalenes (**1a—g**) are of interest from the point of view of the search for biologically active compounds, since they are the structural analogs of known antitumor agents, for example, AG 331 (see Ref. 1). Earlier, we have developed a number of methods for the synthesis of these compounds.$^{2-5}$ These methods have the disadvantage of using polyphosphoric acid (PPA) as a solvent, and, as a consequence, difficulties in handling scaled amounts of reagents. In the present work, we suggest a *one pot* method for the synthesis of compounds **1a—g**, which has no such a disadvantage. It is based on the following sequence: the azo-coupling of carbonyl compounds **2a—g**, the reduction of the intermediate azo compounds **3a—g**, and the heterocyclization of the intermediate amines **4a—g** (Scheme 1).

The total yields were 34—47%.

Scheme 1



R = Me, R´ = H (**a**); R = H, R´ = Me (**b**); R = R´ = Me (**c**); R = Ph, R´ = Me (**d**); R = H, R´ = Ph (**e**); R = Me, R´ = Ph (**f**); R = R´ = Ph (**g**); Ar = 4-$O_3SC_6H_4$

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* Dedicated to Academician of the Russian Academy of Sciences I. P. Beletskaya on the occasion of her anniversary.

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Synthesis of 1*H*-1,5,7-triazacyclopenta[*c,d*]phenalenes (general procedure). A mixture of the corresponding 6(7)-formyl(acyl)perimidine (**2a—g**) (1 mmol), diazobenzenesulfonic acid (0.276 g, 1.5 mmol), and sodium acetate (0.164 g, 2 mmol) in acetic acid (10 mL) was vigorously stirred at room temperature for 1 h, then heated to 50 °C over 15 min, followed by the addition of zinc dust (0.32 g, 5 mmol) and reflux for 1 h with stirring. The reaction mixture was cooled to 80 °C, poured into a stirred cold water (30 mL), pH was raised to ~8. A precipitate formed was filtered off, the mother liquor was extracted with benzene (3×50 mL), the precipitate was dried and extracted in a Soxhlet extractor with benzene (100 mL) over 3 h. The benzene phases were combined, the solvent was evaporated. The compounds obtained were purified by recrystallization.

NMR spectra were recorded on a Bruker WP-200 (200 MHz) spectrometer, using $SiMe_4$ as an internal standard. The reaction progress and individuality of the compounds synthesized were monitored by TLC on Silufol UV-254 plates, using the 1 : 1 ethyl acetate—ethanol solvent system as the eluent. Diazobenzenesulfonic acid was obtained by the known method.[6] 6(7)-Formyl(acyl)perimidines were obtained according to the procedures described earlier.[7,8]

6-Methyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1a). The yield was 0.07 g (34%). M.p. 237—238 °C (from benzene; Ref. 4: m.p. 237—238 °C). ^{1}H NMR spectrum is similar to that given in the work.[4]

2-Methyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1b). The yield was 0.083 g (40%). M.p. 259—260 °C (from benzene; Ref. 2: m.p. 259—260 °C). ^{1}H NMR spectrum is similar to that given in the work.[2]

2,6-Dimethyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1c). The yield was 0.102 g (46%). M.p. 271—272 °C (from benzene; Ref. 2: m.p. 271—272 °C). ^{1}H NMR spectrum is similar to that given in the work.[2]

2-Methyl-6-phenyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1d). The yield was 0.133 g (47%). M.p. 245—246 °C (from benzene with light petroleum; Ref. 4: m.p. 245—246 °C). ^{1}H NMR spectrum is similar to that given in the work.[4]

2-Phenyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1e). The yield was 0.121 g (45%). M.p. 263—265 °C (from benzene; Ref. 4: m.p. 263—265 °C). ^{1}H NMR spectrum is similar to that given in the work.[4]

6-Methyl-2-phenyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1f). The yield was 0.116 g (41%). M.p. 291—292 °C (from benzene; Ref. 4: m.p. 291—292 °C). ^{1}H NMR spectrum is similar to that given in the work.[4]

2,6-Diphenyl-1*H*-1,5,7-triazacyclopenta[*c,d*]phenalene (1g). The yield was 0.135 g (39%). M.p. 169—171 °C (from benzene with light petroleum; Ref. 4: m.p. 169—171 °C). ^{1}H NMR spectrum is similar to that given in the work.[4]

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