Letters to the Editor

New *one-pot* reaction of perimidines with nitroethane and acylating agents in polyphosphoric acid*

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A structural framework of [*c*,*d*]-annulated indoles is encountered with in nature and synthetic compounds, exhibiting various biological activity.[1—3] Low toxic polyheterocyclic analogs of acenaphthenes and benzopyrenes can in prospects replace these widely used photochemical probes,[4] making them more attractive for medical application. Besides, such structures can be used in nanotechnology for modeling reactivity of azafullerenes[5] and atom-modified nanotubes.[6]

Earlier, we have described a number of methods for *peri*-annulation of pyrrole ring.[7—12] These methods have some disadvantages: some of them require preliminary functionalization of perimidine,[11,12] other use sodium azide, which in acidic medium can form highly toxic and explosive hydrazoic acid.[7—10] In the present work, we suggest two approaches to the synthesis of such compounds, which do not have the disadvantages mentioned above. These approaches are based on the reaction recently discovered in our laboratory,[13—15] electrophilic acetamidation of arenes with nitroethane in polyphosphoric acid (PPA)**

We showed that the reaction of 1 mmol of perimidines **1a—c** and 2 mmol of nitroethane (Scheme 1) in 2—3 g PPA at 100—105 °C for 5 h (monitoring by thin-layer chromatography) with subsequent addition of 1.5 mmol of the corresponding 1,3,5-triazine **3** and heating for another 3 h at 110—120 °C (**3b**,**c**) or 90—100 °C (**3a**) leads to 1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalenes **5a—i** in 36—51% yield.

It is probable that the reaction proceeds through the acetamidation of perimidines **1a—c** with the formation of acetamides **2a—c** (see Ref. 15), which through the reaction with 1,3,5-triazines, successive ring opening and heterocyclization are converted to the intermediate *N*-acetyl derivatives **4a—i**. Similar processes involving 1,3,5-triazines in PPA are considered in details in the review.[17] Compounds **4a—i** undergo hydrolysis after treatment of the reaction mixture with water to give indoles **5a—i**.

We showed that more available carboxylic acids can be used instead of 1,3,5-triazines for the preparation of compounds **5d—i** by this reaction (Scheme 2), with the yields remaining on the same level.

The mechanism is similar to that described above.

In conclusion, we have developed two method for the synthesis of 1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalenes **5a—i** based on the reaction of perimidines

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** Polyphosphoric acid containing 86% of P_2O_5 was obtained according to the known procedure (see Ref. 16).

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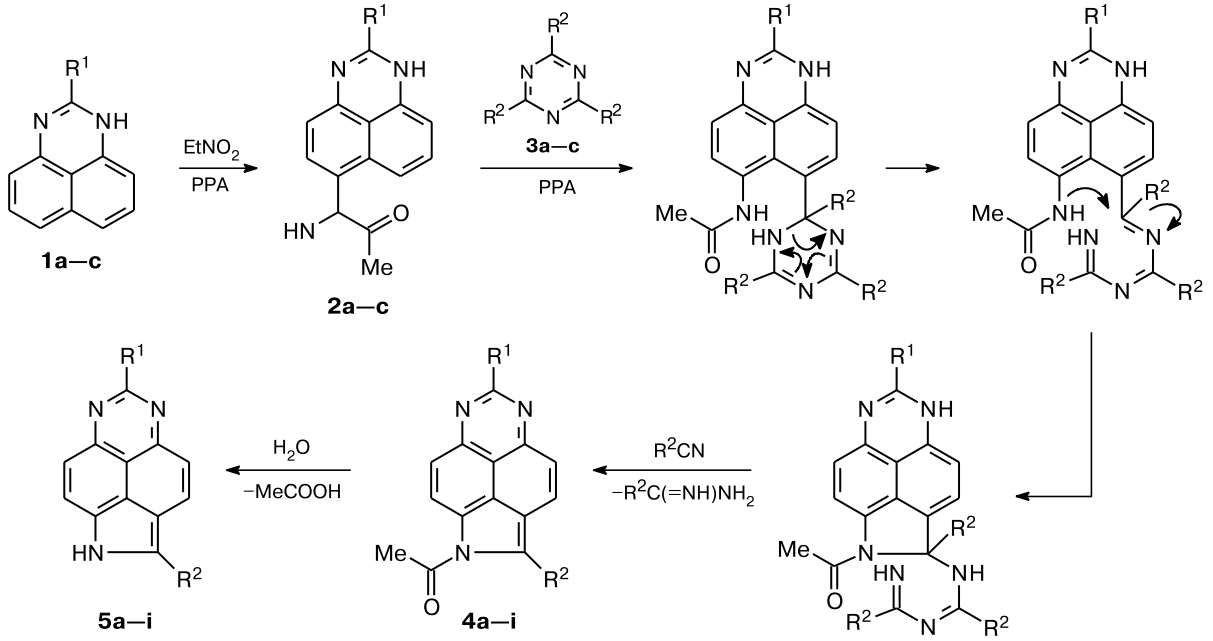
Scheme 1



1—3: $R^1 = R^2$ = H (**a**), Me (**b**), Ph (**c**)

Starting compounds	Product	R^1	R^2	Starting compounds	Product	R^1	R^2	Starting compounds	Product	R^1	R^2
1a, **3a**	**4a**, **5a**	H	H	**1a**, **3b**	**4d**, **5d**	H	Me	**1a**, **3c**	**4g**, **5g**	H	Ph
1b, **3a**	**4b**, **5b**	Me	H	**1b**, **3b**	**4e**, **5e**	Me	Me	**1b**, **3c**	**4h**, **5h**	Me	Ph
1c, **3a**	**4c**, **5c**	Ph	H	**1c**, **3b**	**4f**, **5f**	Ph	Me	**1c**, **3c**	**4i, 5i**	Ph	Ph

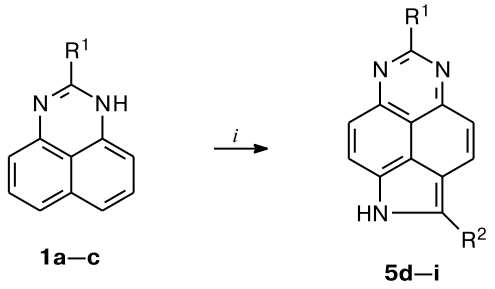
with nitroethane and 1,3,5-triazines or carboxylic acids in PPA.

^{1}H NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz), using $SiMe_4$ as an internal standard. Reaction progress and individuality of synthesized compounds were monitored by chromatography on Silufol UV-254 plates, using a 1 : 1 ethyl acetate—ethanol solvent system. Nitroethane, 1,3,5-triazine, 2,4,6-triphenyl-1,3,5-triazine, acetic and benzoic acids are commercial agents (Aldrich). Perimidine,[18] 2-methyl- and 2-phenylperimidine,[18] and 2,4,6-trimethyl-1,3,5-triazine[19] were obtained according to the described procedures.

Synthesis of triazacyclopentaphenalenes 5a—i (general procedure). A mixture of the corresponding perimidine **1a—c** (1 mmol) and nitroethane (0.15 g, 2 mmol) in PPA (2—3 g) was heated at 100—105 °C for 3 h (TLC monitoring). Then, the corresponding 1,3,5-triazine or carboxylic acid (1.5 mmol) was added and the mixture was allowed to stand for 5 h at 110—120 °C (**3b**,**c**) or 90—100 °C (**3a**). The reaction mixture was cooled to 80 °C, poured into cold water (30 mL) with stirring, aqueous ammonia was used to bring the pH to ~8, a precipitate formed was filtered off, the mother liquor was extracted with benzene (3×50 mL), a precipitate was dried and extracted in a Soxhlet extractor with benzene (100 mL) for 3 h. The benzene fractions were combined, the solvent was evaporated. Compounds obtained were purified by recrystallization.

1*H*-1,5,7-Triazacyclopenta[*c*,*d*]phenalene (5a). The yield was 0.081 g (42%), m.p. 207—209 °C (benzene). The data in Ref. 7: m.p. 207—209 °C. NMR spectrum agrees with that described in the work.[7]

Scheme 2



i.1) $EtNO_2$/PPA; 2) R^2COOH; 3) H_2O.

6-Methyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5b). The yield was 0.106 g (51%), m.p. 237—238 °C (benzene). The data in Ref. 7: m.p. 237—238 °C. NMR spectrum agrees with that described in the work.[7]

6-Phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5c). The yield was 0.105 g (39%), m.p. 201—203 °C (benzene). The data in Ref. 7: m.p. 201—203 °C. NMR spectrum agrees with that described in the work.[7]

2-Methyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5d). The yield was 0.079 g (38%) (from 2,4,6-trimethyl-1,3,5-tri-

azine), 0.085 g (41%) (from acetic acid), m.p. 259—260 °C (from benzene). The data in Ref. 7: m.p. 259—260 °C. NMR spectrum agrees with that described in the work.[7]

2,6-Dimethyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5e). The yield was 0.104 g (47%) (from 2,4,6-trimethyl-1,3,5-triazine), 0.106 g (48%) (from acetic acid), m.p. 271—272 °C (from benzene). The data in Ref. 7: m.p. 271—272 °C. NMR spectrum agrees with that described in the work.[7]

2-Methyl-6-phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5f). The yield was 0.13 g (46%) (from 2,4,6-trimethyl-1,3,5-triazine), 0.139 g (49%) (from acetic acid), m.p. 245—246 °C (from benzene with light petroleum). The data in Ref. 7: m.p. 245—246 °C. NMR spectrum agrees with that described in the work.[7]

2-Phenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5g). The yield was 0.097 g (36%) (from 2,4,6-triphenyl-1,3,5-triazine), 0.121 g (41%) (from benzoic acid), m.p. 263—265 °C (from benzene). The data in Ref. 7: m.p. 263—265 °C. NMR spectrum agrees with that described in the work.[7]

2-Phenyl-6-methyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5h). The yield was 0.13 g (46%) (from 2,4,6-triphenyl-1,3,5-triazine), 0.136 g (48%) (from benzoic acid), m.p. 291—292 °C (from benzene). The data in Ref. 7: m.p. 291—292 °C. NMR spectrum agrees with that described in the work.[7]

2,6-Diphenyl-1*H*-1,5,7-triazacyclopenta[*c*,*d*]phenalene (5i). The yield was 0.148 g (43%) (from 2,4,6-triphenyl-1,3,5-triazine), 0.159 g (46%) (from benzoic acid), m.p. 169—171 °C (from benzene with light petroleum). The data in Ref. 7: m.p. 169—171 °C. NMR spectrum agrees with that described in the work.[7]

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