Syntheses and Reactions of Amino- and Azidophenalenones

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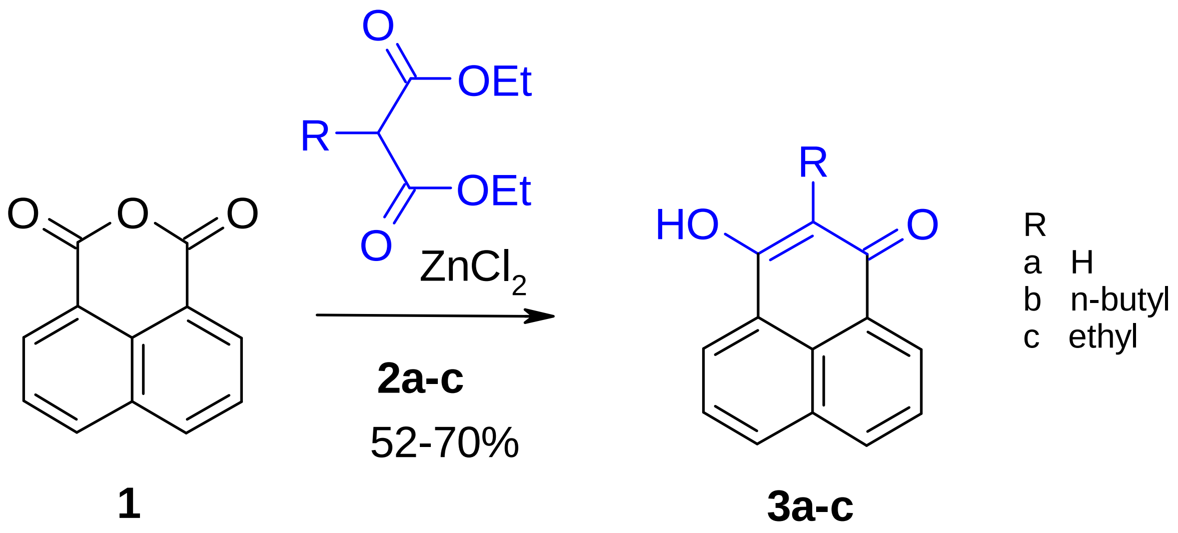
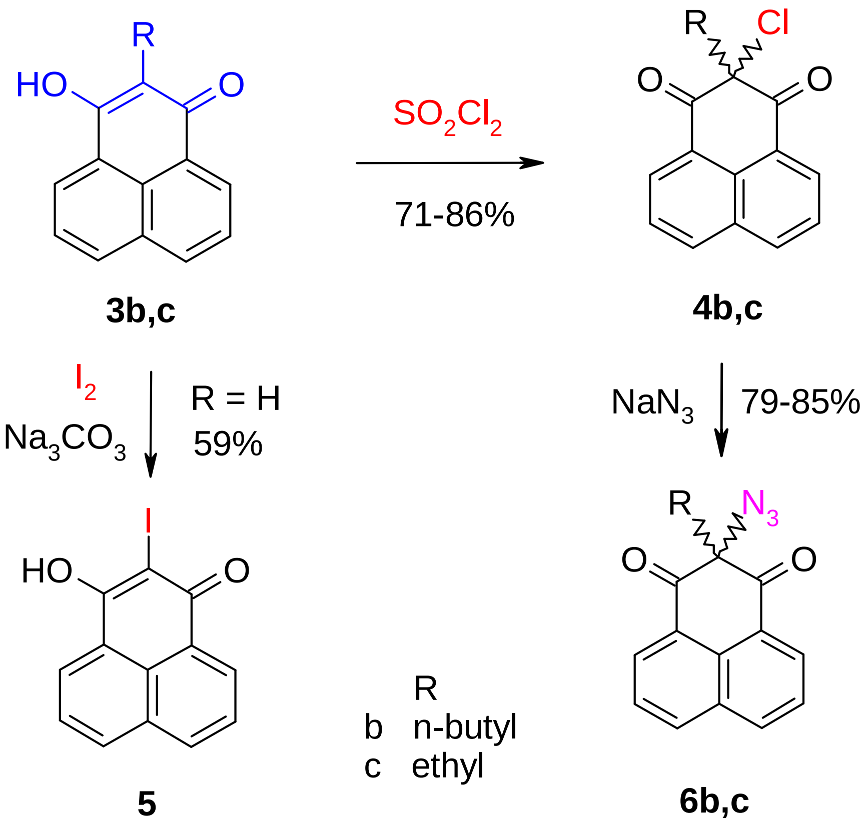
Synthesis of 3-hydroxyphenalenones 3.



3-Hydroxyphenalenones **3** were synthesized from 1,8-naphthalic anhydride **1** and malonates **2** with anhydrous zinc chloride as condensation agent.

1. Electrophilic halogenation to 4 and 5.
Azidation to azidophenalenediones 6.



3-Hydroxyphenalenones react by electrophilic halogenation to 2-chlorophenalenediones **4** or 2-iodophenalenone **5**.

The chloro group of **4** was exchanged against azide by reaction with sodium azide to give 2-azidophenalenediones **6**.

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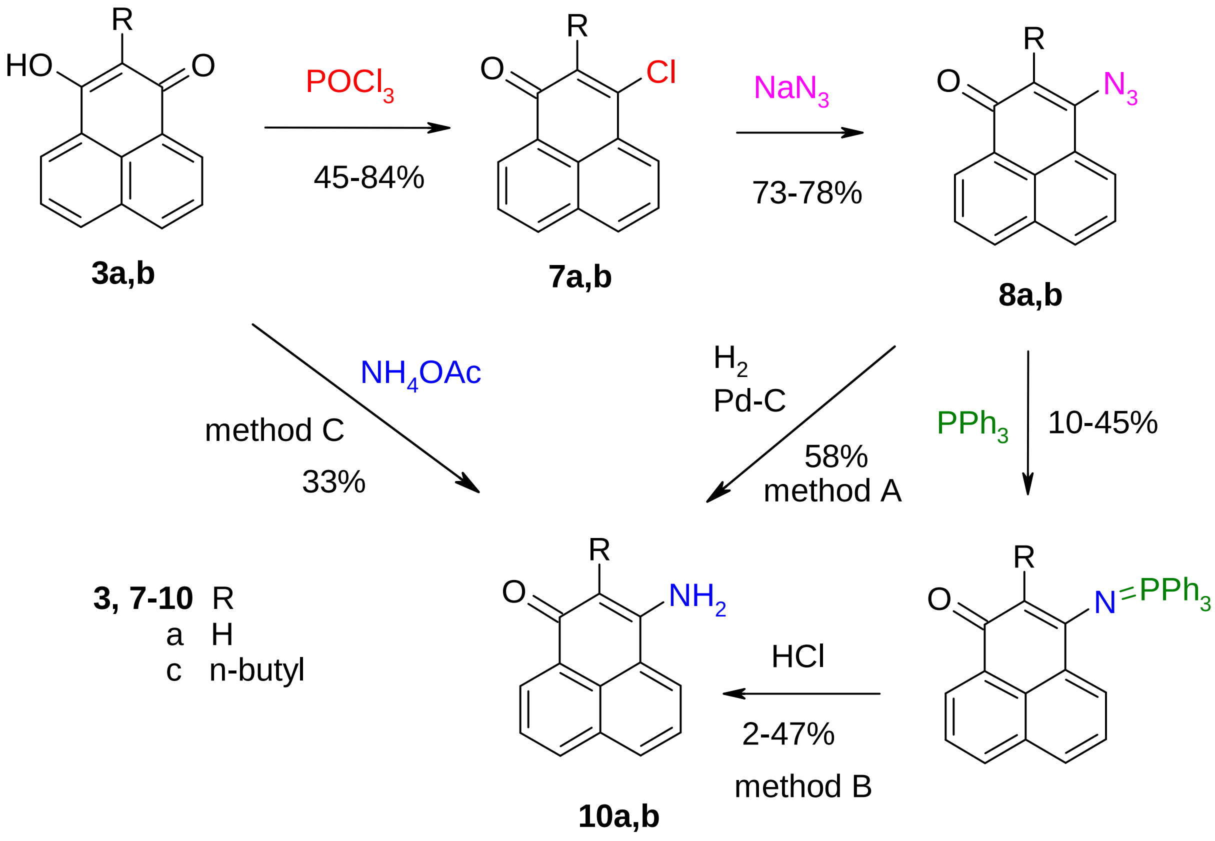
2. Nucleophilic chlorination of 3-hydroxyphenalenones 3. Formation of 3-azido- and 3-aminophenalenones 8 and 10.

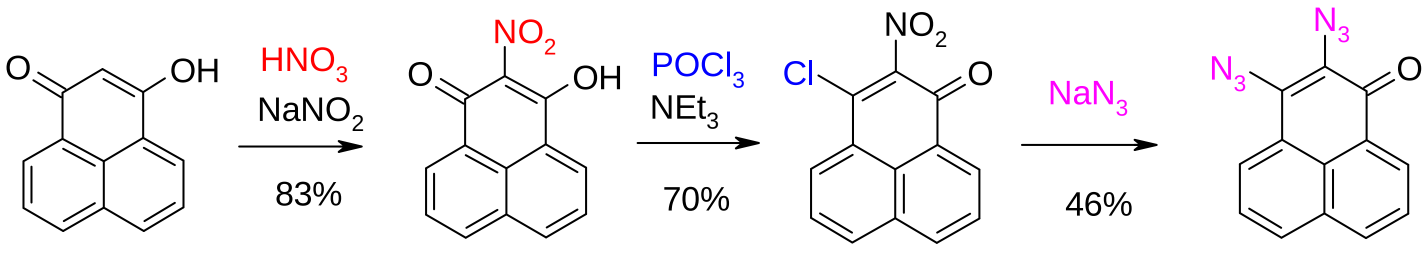


Nucleophilic chlorination of **3** furnishes 3-chlorophenalenones **7**, which were converted to 3-azidophenalenones **8**.

Staudinger reaction of **8** with triphenylphosphane gave phosphazenes **9** which hydrolyzed in acidic media to 3-aminophenalenones **10**.

Amines **10** can also be obtained directly from 3-hydroxy-phenalenones **3** and ammonium acetate, or by catalytic hydro-genolysis of azides **8**.

3. Introduction of azido substituents into 1-chloro-2-nitrophenalenone (12)



3a **11** **12** **13**

Nitration of 3-hydroxyphenalenone **3a** with nitric acid forms 2-nitrophenalenone **11**, which was converted to 3-chloro-2-nitrophenalenone **12**.

Attempts to introduce the 3-azido group in **12**, however, resulted in an exchange of both, the nitro group and the chloro group, to form 2,3-diazidophenalenone **13**.

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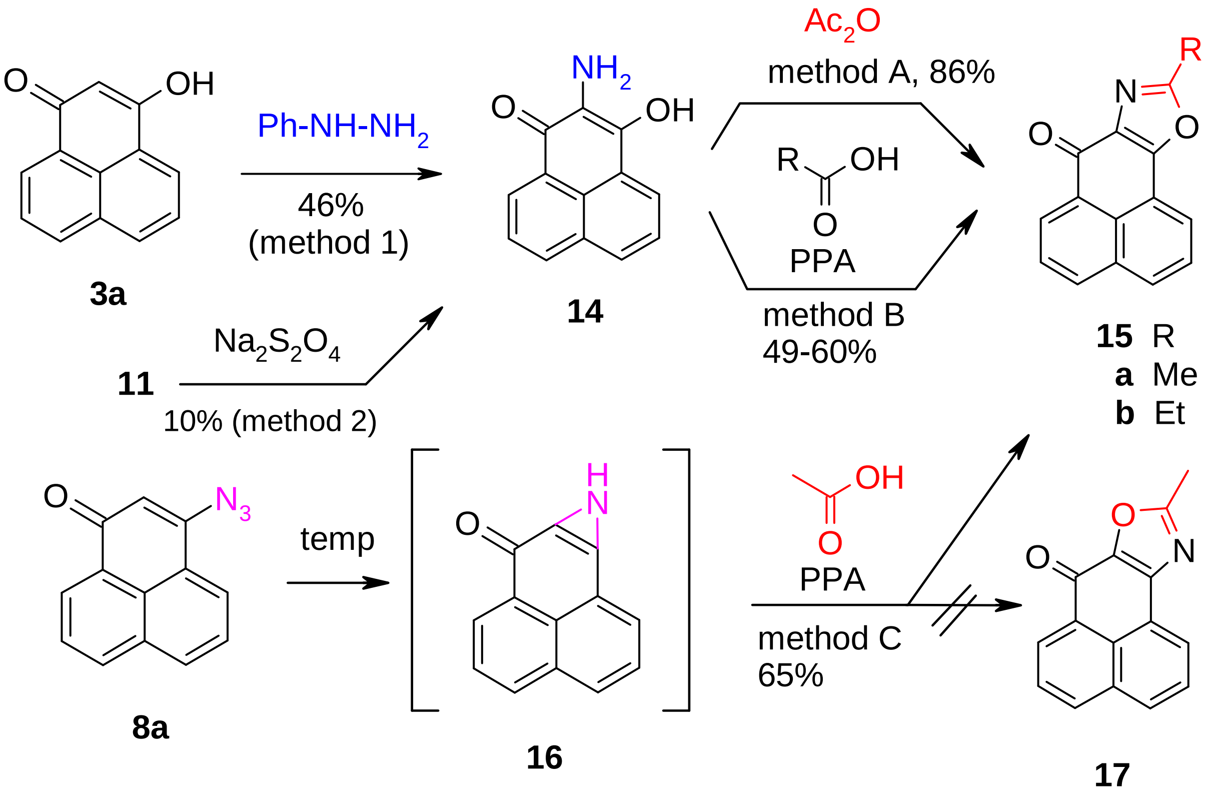
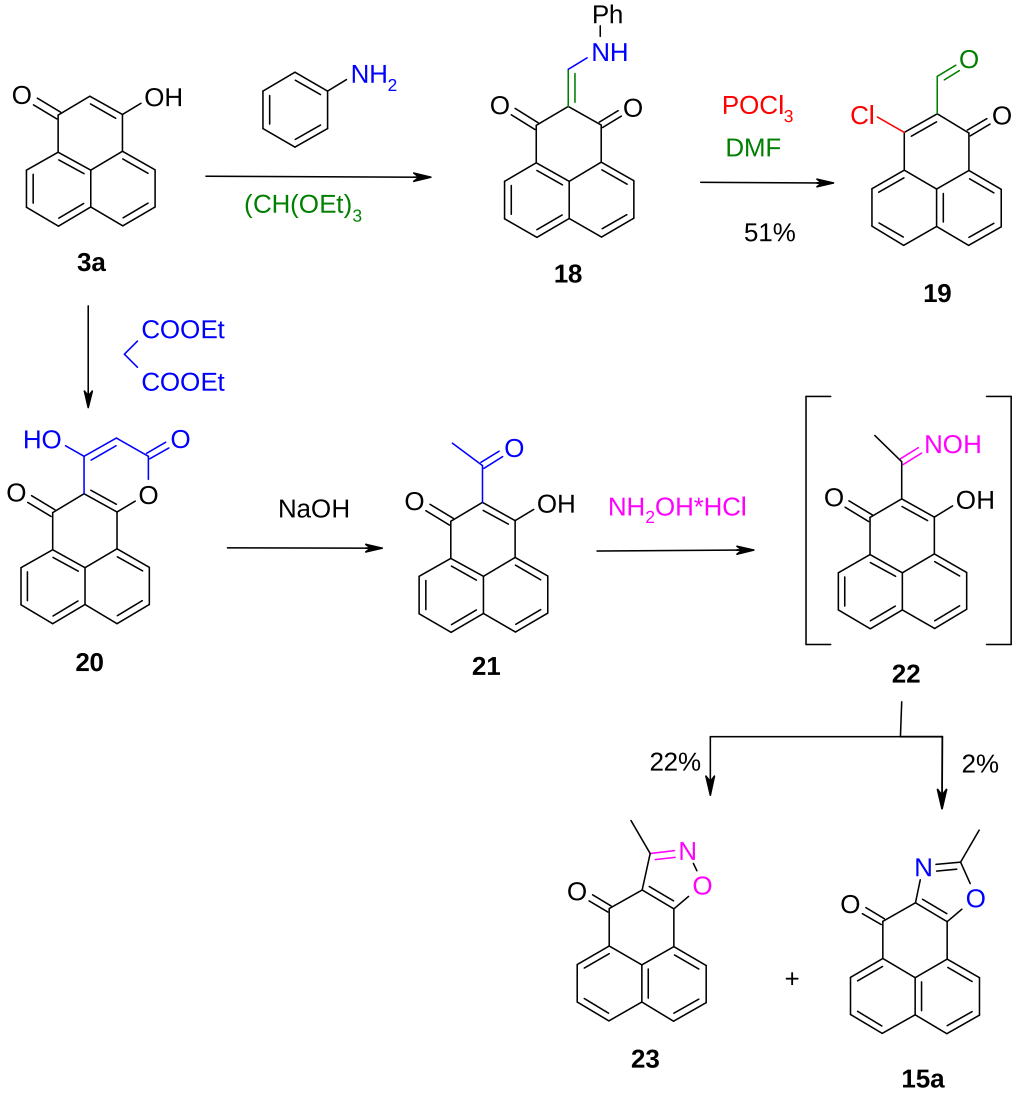
4. Cyclization reactions of 2-amino-3-hydroxyphenalenone 14 and 3-azidophenalenone 8a to phenaleno[2,1-*d*]oxazol-7-ones 15



2-Amino-3-hydroxyphenalenone **14** cyclizes with carboxylic acid derivatives to oxazolo-phenalenones **15**

15 was also obtained from 3-azidophenalenone **8a** and a carboxylic acid involving an azirine intermediate **16**. This intermediate allows to move the position of the N-atom.

5. Cyclization reaction of 2-acetyl-3-hydroxyphenalenone 21 to phenaleno[2,1-*d*]oxazol-7-one 15 and phenaleno[2,1-*d*]isoxazol-7-one 23



Another cyclization reaction leads via the intermediate oxime **22** of 2-acetylphenalenone **21**,

22 gives an isomer mixture of isoxazolophenalenone **23** as main product and oxazolophenalenone **15** as by-product, because of a parallel reaction via a *Beckmann* rearrangement.

Conclusion

3-Hydroxyphenalenones **3** are electrophilically halogenated at position 2 to give 2-chlorophenalenones **4**, and nucleophilically halogenated at position 3 to form 3-chlorophenalenones **7**, **12** and **19**.

Chloro substituents can be exchanged against an azido group to form 2-azides **6** and 3-azides **8**. Azidation of 3-chloro-2-nitrophenalenone **12** gave 2,3-diazidophenalenone **13** by exchange of both the nitro group and the chloro group.

3-Aminophenalenones **10** are formed either directly from **3**, or from 3-azidophenalenones **8** by catalytic hydrogenolysis, or by a *Staudinger* reaction via phosphazenes **9**.

2-Amino-3-hydroxyphenalenone **14** cyclizes with carboxylic acid derivatives to oxazolo-phenalenones **15**, which were also obtained from 3-azidophenalenone **8a** and a carboxylic acid involving an azirine intermediate **16**.

Another way for the such heterocycles leads via the intermediate oxime **22** of 2-acetylphenalenone **21**, which gives an isomer mixture: main product was the isoxazole **23**, as a by-product the isomer oxazole **15** is formed via a *Beckmann* rearrangement.