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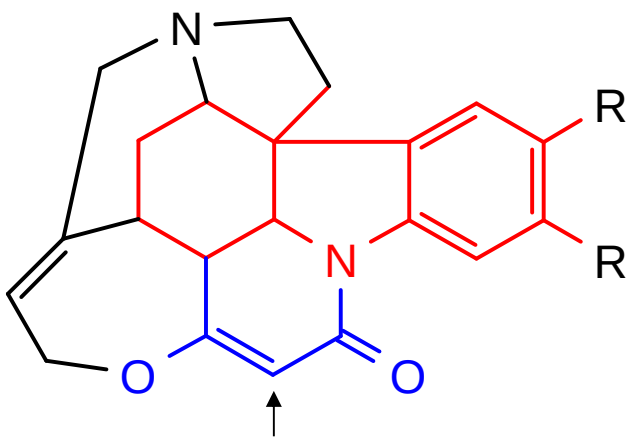
Syntheses and Reactions of 5-Unsubstituted 11b-Methyl-1,2,3,11b-tetrahydro-pyrido[3,2,1-*jk*]carbazoles Having a Strychnos Alkaloids Partial Structure



The structure of tetrahydropyrido[3,2,1-*jk*]carbazol-6-one (**colored partial structure**) is found in the heterocyclic skeleton of many natural products (e. g. **Strychnos alkaloids**). It contains the biological interesting combination of the well-known **indole** structure (**red** in combination as carbazole) and the **4-hydroxy-2-pyridone** structure (**blue**). The 5-unsubstituted position (arrow-marked) allows the instroduction of a series of interesting substituents.

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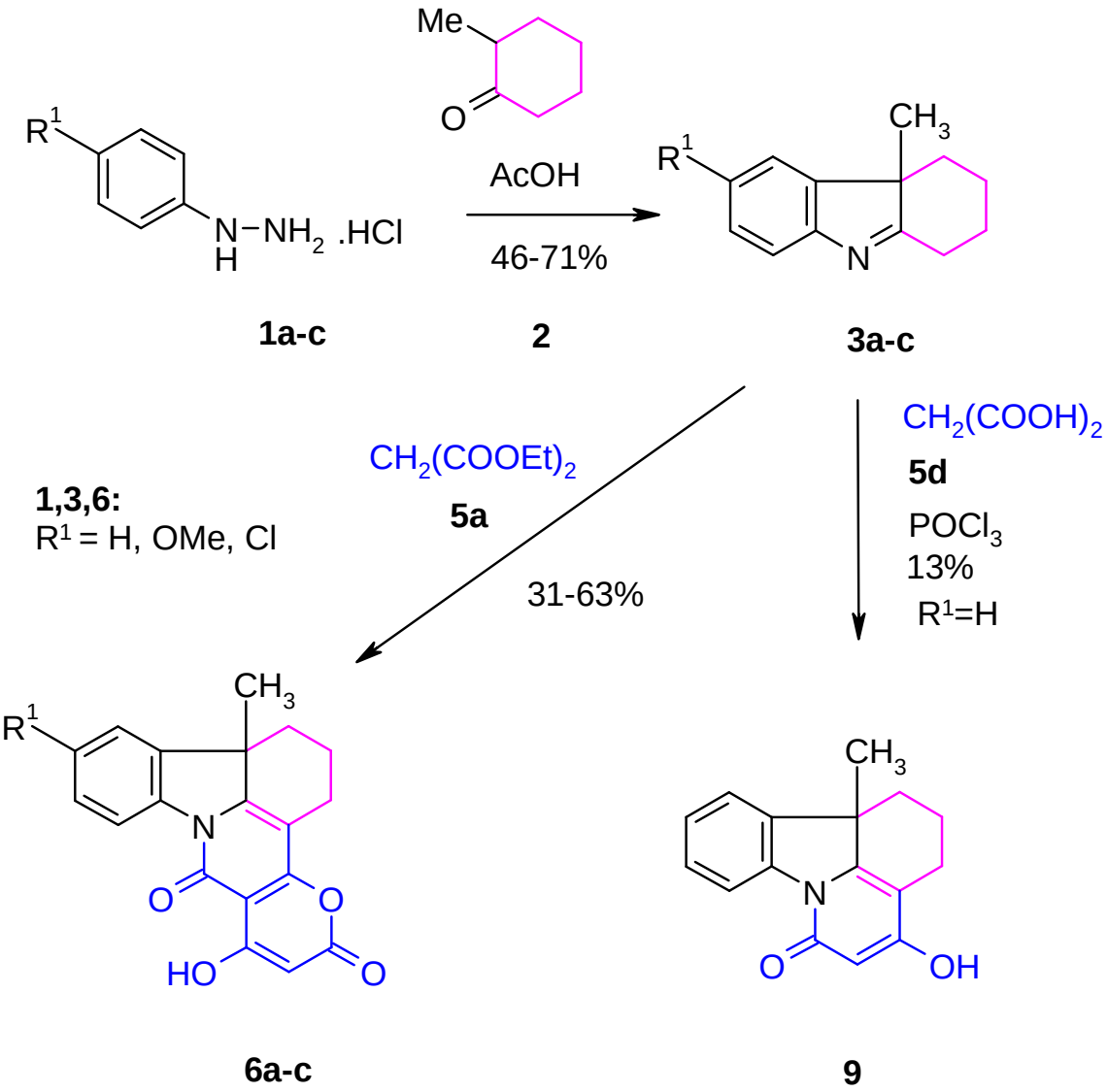

Tetrahydrocarbazoles **3**, obtained from hydrazones **1** and 2-methylcyclohexanone **2**, react with malonic acid/$POCl_3$ directly, but in low yields, to tetrahydro-pyrido[3,2,1-*jk*]carbazol-6-one **9**.

The condensation of **3a-c** with diethylmalonate **5a** leads to pyrano[2',3':4,5]pyrido[3,2,1-*jk*]carbazole-5,8-diones **6**, which can serve as precursors for the synthesis of **9**.

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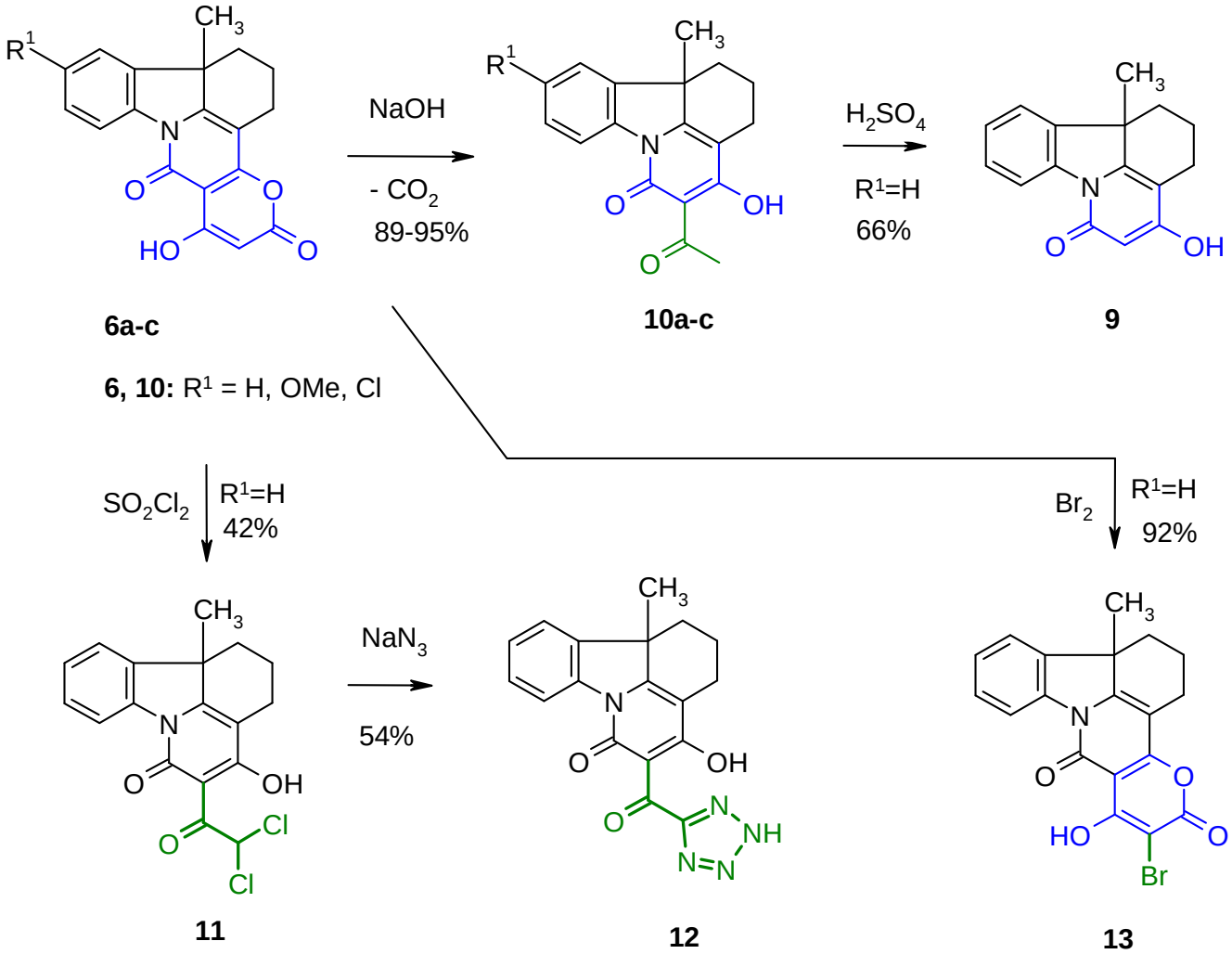

Alkaline degradation of pyrones **6** form by decarboxylation 5-acetyl-pyridocarbazoles **10**, which can be deacetylated to **9** with 90% sulfuric acid. The ring opening of **6** with sulfurylchloride forms the dichloroacetyl compound **11**, which reacts with sodium azide to 5-tetrazolylcarbonyl-pyridocarbazole **12**. Bromination of **6** forms a single brominated pyrone **13**.

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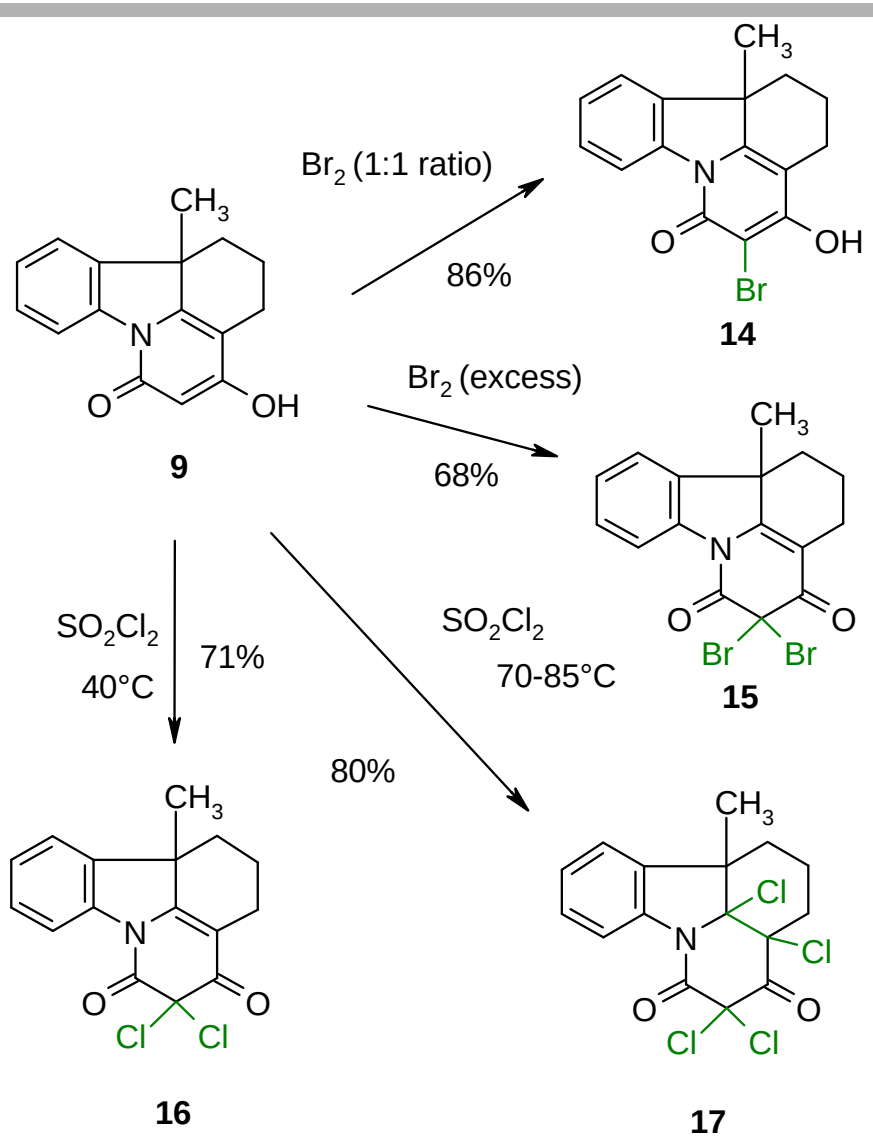

Electrophilic bromination of pyrido-carbazole **9** gives 5-mono- and 5,5-dibromo products **14** and **15**, depending on the reaction conditions. With sufuryl chloride below 40 °C, 5,5-dichloro-pyridocarbazoledione **16** was formed. Higher reaction temperatures resulted in an additional halogenation at the isolated double bond at the 3a,11c-position and produced 3a,5,5,11c-tetrachloro-pyridocarbazoledione **17**.

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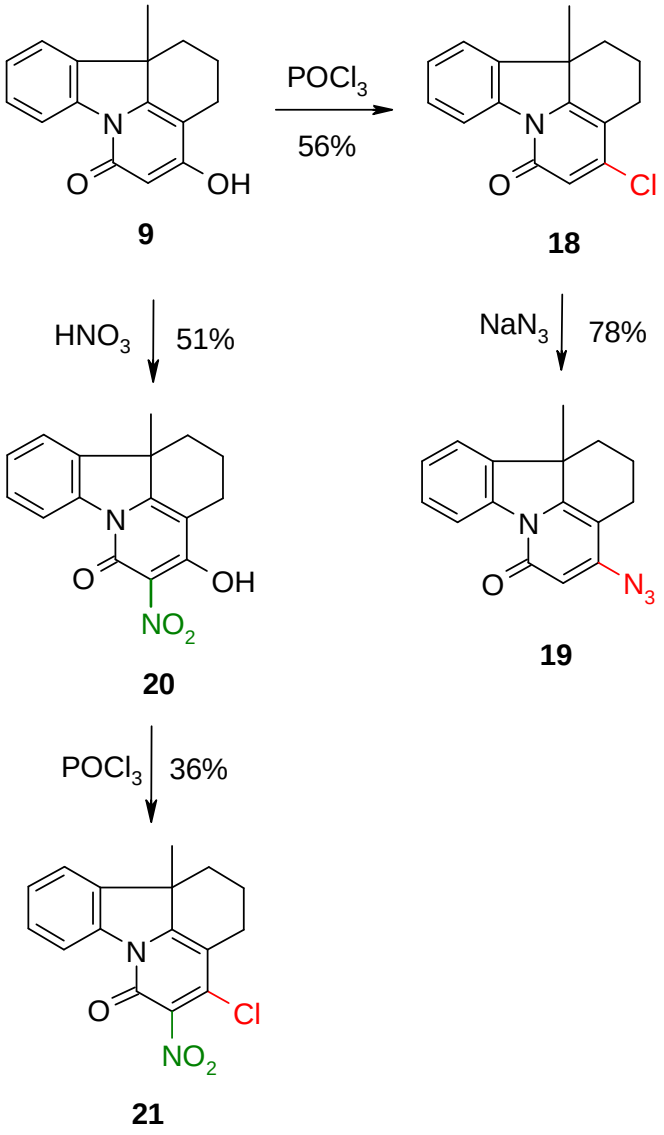

Nucleophilic exchange of the hydroxy group in **9** leads with phosphoryl chloride to 4-chloro-pyridocarbazole **18**. A further nucleophilic exchange in **18** with sodium azide produces 4-azido-pyridocarbazole **19**.

Nitration of **9** with nitric acid/sodium nitrite gives 5-nitro-pyridocarbazole **20**, which can be chlorinated with phosphoryl chloride using triethylamine as catalyst and formed 4-chloro-5-nitro compound **21** in moderate yields.

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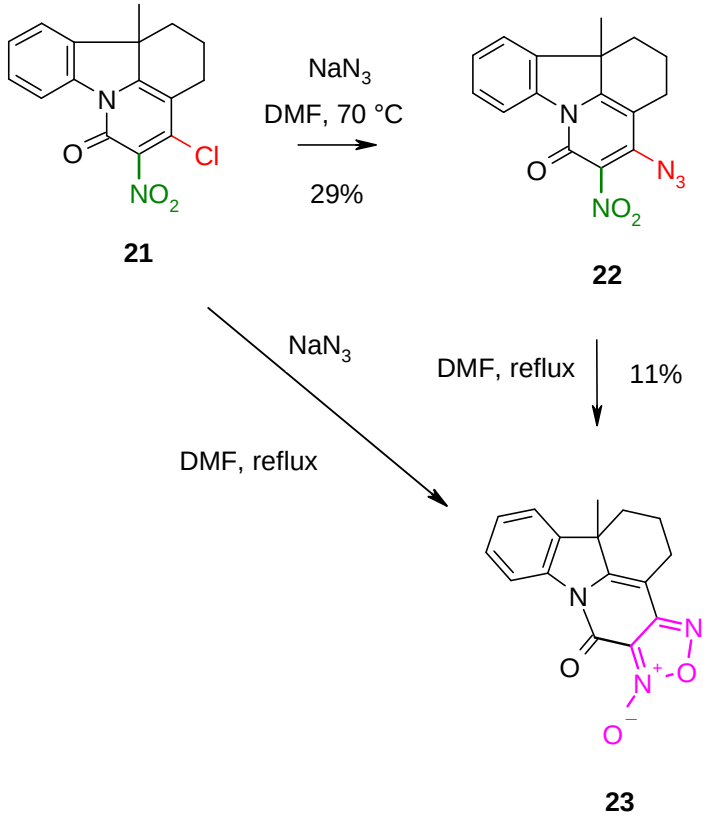

In the last years we investigated a series of cyclization reactions of azides with reactive ortho-substituents. The reaction conditions of the ring closure reaction of the 4-azido-5-nitro derivative **22** were investigated by differential scanning calorimetry (DSC). From these diagrams the information on the cyclization temperature to form furoxane **23** was obtained which allows to obtain both, a pure azido compound **22** from chloro derivative **21** without decomposition to furoxano–pyridocarbazole **23**, and a smoth cyclization reaction from **22** to furoxane **23**.

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Conclusion

4a-Methyl-2,3,4,4a-tetrahydro-1*H*-carbazoles **3** were shown to cyclize with diethylmalonate **5a** to pyranopyridocarbazole-5,8-diones **6**, which can be degraded in a two-step reaction via an acetyl intermediate **10** to 5-unsubstituted tetrahydropyridocarbazolones **9**. Attempts to use shorter reaction pathways gave too low yields of tetrahydropyridocarbazolones **9**.

Electrophilic substitution of tetrahydropyridocarbazolones **9** was shown to take place mainly at position 5 and produces 5-bromo, 5,5-dibromo- and 5,5-dichloro derivatives **14**, **15** and **16**. Nitration affords 5-nitroderivative **20**. Nucleophilic substitution results in the exchange of the 4-hydroxy-group against a chloro- or an azido group to afford derivatives **18**, **19**, **21** and **22**.

Thermal cyclization of 4-azido-5-nitro-tetrahydropyridocarbazolone **22** was investigated by differential scanning calorimetry (DSC) and produced furoxano-pyridocarbazole **23** under suitable conditions obtained from DSC data..