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Interesting Synthetic Approaches Towards [1]Benzopyrano[4,3-*b*]quinolines *via* Intramolecular Reaction of Nitrilium Salts

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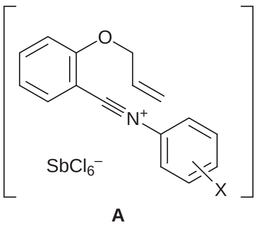
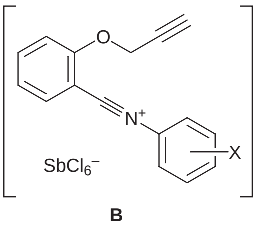
The *o*-allyloxybenzanilides **2a**,**b**,**d** and *o*-propargyloxybenzanilides **3a–f** are prepared and converted to the corresponding dihydro[1]benzopyrano[4,3-*b*]quinolinium hexachloroantimonate **6a** and [1]benzopyrano[4,3-*b*]quinolines **9a–e**, **10** upon treatment with PCl$_5$ followed by SbCl$_5$.

Much attention has been directed to the synthesis of quinolines and their derivatives as many naturally occurring quinolines are known for their interesting diverse applications.[1,2] Thus, specially designed quinolines have found applications in different fields including chemistry, polymer science, pharmaceuticals, veterinary products, agrochemicals and reagents for quantitative and qualitative analysis.[1,2] Meerwein *et al.*[3] first described the conversion of *N*-arylnitrilium salts to quinazolinium salts *via* their reaction with nitriles. With acetylenes instead of nitriles quinolinium salts are produced.[4–6] Recently, Jochims and coworkers[7] reviewed these reactions and also studied carefully the different reactions between nitrilium salts and nucleophilic alkenes in the presence of Lewis acids.[7,8] Thus, depending on the structure of the alkene used, the reactions with *N*-arylnitrilium salts were found to lead to dihydroquinolinium salts (*via* formal Diels–Alder reaction), ene reaction, Hoeben–Hoesch reaction or $2+2$ cycloaddition.[7,8] Also, it has been shown in these studies that no action takes place between *N*-arylnitrilium salts and vinyl chloride, allyl bromide or allyl chloride (less nucleophilic alkenes).[7]

The previous results prompted us to investigate a potential synthetic route towards [1]benzopyrano[4,3-*b*]quinolines and their dihydro derivatives by application of an intramolecular cycloaddition reaction of nitrilium salts *via* a formal intramolecular Diels–Alder reaction with suitably located allyloxy and propargyloxy groups. This synthetic strategy depends on treatment of the appropriate imidoyl chlorides **4**, **5** with a Lewis acid to give the corresponding *N*-aryl-*o*-allyloxybenzonitrilium salts **A** and *N*-aryl-*o*-propargyloxybenzonitrilium salts **B**.



A



B

The synthetic routes followed towards the target 6*H*-[1]benzopyrano[4,3-*b*]quinoline and its dihydro derivatives are outlined in Scheme 1. Thus, alkylation of *N*-arylsalicylamides **1a–f** (readily available by the reaction of salicylic acid or its derivatives with the appropriate arylamine)[9] with allyl bromide or propargyl bromide in basic medium afforded the corresponding *o*-allyloxybenzanilides **2a**,**b**,**d** and *o*-propargyloxybenzanilides **3a–f** respectively in good yields. Heating each of compounds **2a**,**b**,**d** and **3a–f** with phosphorus pentachloride in benzene afforded the corresponding imidoyl chlorides **4a**,**b**,**d**, **5a–f**.

Treatment of *N*-phenyl-*o*-allyloxybenzimidoyl chloride **4a** with antimony pentachloride at −25 °C to room temperature afforded the corresponding 6*H*-6*a*,7-dihydro[1]benzopyrano[4,3-*b*]quinolinium hexachloroantimonate **6a**. On the other hand, similar treatment of the *p*-chloro and *p*-methoxy derivatives **4b**,**d** led, instead of the expected derivatives **6b**,**d**, to the corresponding 6*H*-[1]benzopyrano[4,3-*b*]quinolinium hexachloroantimonates **7b**,**d**. The latter reaction proceeded *via* dehydrogenation which might be facilitated by the substituent in the initially formed dihydroquinolinium salts. Also, leaving a solution of compound **6a** in (CD$_3$)$_2$SO at room temperature overnight led to the partial formation (*ca.* 50%) of the corresponding quinolinium derivative **7a**. However, compound **6a** is stable for more than two months in the solid state in a closed dark bottle.

Treatment of *N*-aryl-*o*-propargyloxybenzimidoyl chlorides **5a–f** with antimony pentachloride at −25 °C to room temperature afforded the corresponding 6*H*-[1]benzopyrano[4,3-*b*]quinolinium hexachloroantimonates **7a–e** and **8**. Treatment of the latter in dichloromethane with sodium hydroxide solution afforded the corresponding free bases **9a–e** and **10**. In fact one preliminary report described the conversion of **3a** into **9a** by heating in toluene with phosphorus oxychloride for 48 h.[10] Also, literature offers a synthetic route to the 6-oxo derivatives **11** *via* the reaction of *o*-aminobenzaldehyde and 4-hydroxycoumarin[11,12] or by the reaction of aniline with 3-methylene-3,4-2*H*-dihydrobenzopyran-2,4-dione.[13] Our results offer a general method for a low temperature high yield access to the title ring system that could be of value in parallel and combinatorial synthesis.[14]

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Techniques used: ^{1}H, ^{13}C NMR

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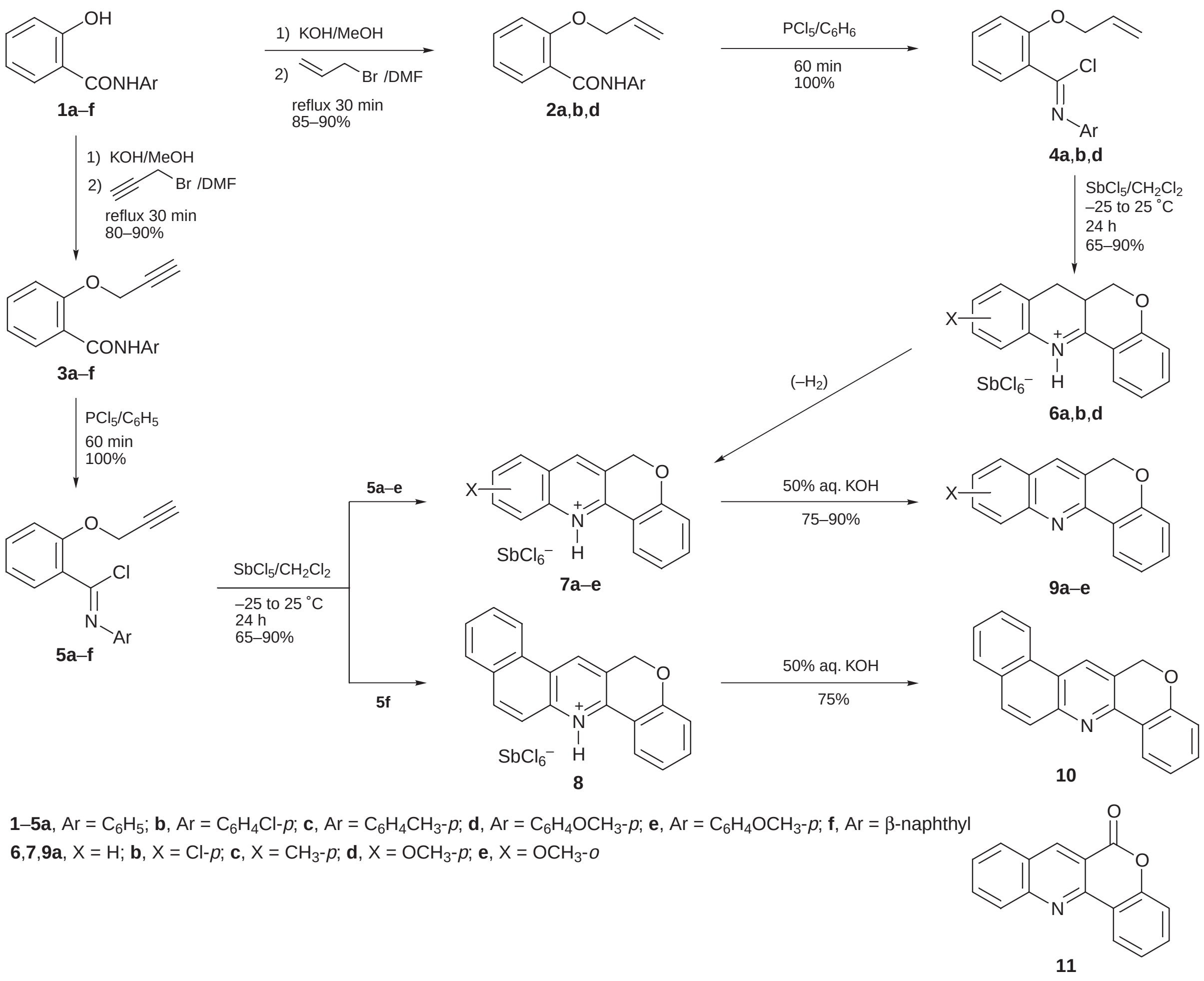

1–5a, Ar = C_6H_5; **b**, Ar = C_6H_4Cl-*p*; **c**, Ar = $C_6H_4CH_3$-*p*; **d**, Ar = $C_6H_4OCH_3$-*p*; **e**, Ar = $C_6H_4OCH_3$-*p*; **f**, Ar = β-naphthyl

6,**7**,**9a**, X = H; **b**, X = Cl-*p*; **c**, X = CH_3-*p*; **d**, X = OCH_3-*p*; **e**, X = OCH_3-*o*

Scheme 1

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