



# Synthesis of 2,2,4-trimethyl-1,2-*H*-dihydroquinoline (TMQ) over selected organosulfonic acid silica catalysts: Selectivity aspects

J. Nowicki<sup>a,\*</sup>, K. Jaroszewska<sup>b</sup>, E. Nowakowska-Bogdan<sup>a</sup>, M. Szmatoła<sup>a</sup>, J. Iłowska<sup>a</sup>

<sup>a</sup> Institute of Heavy Organic Synthesis “Blachownia”, PL47-225 Kędzierzyn-Koźle, Poland

<sup>b</sup> Wrocław University of Science and Technology, Department of Chemistry, PL50-344 Wrocław, Poland

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## ABSTRACT

This paper presents investigation on the synthesis of 2,2,4-trimethyl-1,2-*H*-dihydroquinoline (TMQ) as a result of the reaction of aniline and both acetone and mesityl oxide in the presence of selected sulfonic acid silica catalysts. Condensation of aniline with acetone is very complex process with the formation of significant number of side products, both desirable and undesirable considering the final product (TMQ). In acidic conditions and elevated reaction temperature the reactivity of main raw materials (aniline, acetone) is significantly high, what causes the formation of many side by-products lowering the selectivity of this reaction. In this paper the reaction of aniline with acetone in the presence of heterogeneous acidic silica catalysts were investigated in more detail and discussed. The results were confirmed by GC/MS analysis, that the presence of TMQ isomers and other by-products significantly affected the formation of final product. The formation of previously not described structural isomer of TMQ has been also demonstrated.

## 1. Introduction

Alkyl derivatives of 1,2-*H*-dihydroquinoline (1,2-DHQ) belong to a large group of quinoline derivatives of great practical importance. The most important representative of them is 2,2,4-trimethyl-1,2-*H*-dihydroquinoline known in the market under the acronym TMQ. 2,2,4-Trimethyl-1,2-dihydroquinoline, because of relatively low price and great ease of application, is considered as a very important and effective antioxidant in rubber technologies. The methods of the synthesis of 1,2-quinoline derivatives are based on cyclization reaction well known as Skraup reaction. More detailed studies led to the development of various Skraup-based modifications (Combes, Knorr, Doebner, Friedlander).

The main raw material used in the synthesis of 1,2-dihydroquinoline derivatives is aniline or its alkyl derivatives and detailed variants of the synthesis depend only on the kind of carbonyl component used. As a rule acetone is used, which as a result of sequence reaction condensed with aniline with the formation of 1,2-*H*-dihydroquinoline derivative, i.e. 2,2,4-trimethyl-1,2-*H*-dihydroquinoline (Scheme 1).

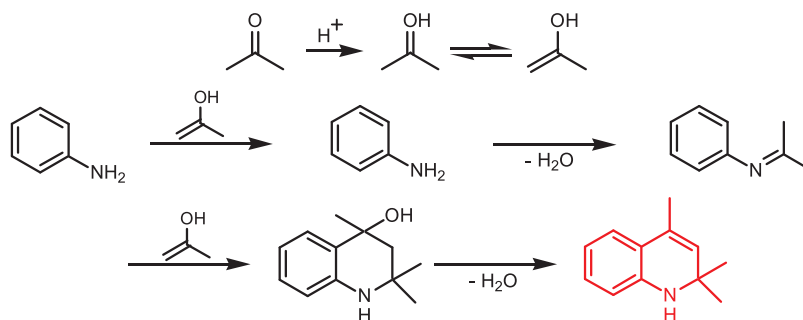
According to Scheme 1 TMQ is manufactured in technical scale. Skraup synthesis of TMQ was described for the first time in 1921 [1]. Later study allow confirmation its chemical structure [2–5]. The synthesis of 1,2-*H*-dihydroquinoline derivatives, according to Skraup method or its various modifications, are carried out mainly in the

presence of homogeneous catalysts. As catalysts most frequently I<sub>2</sub> [1], HCl [6–8], *p*-toluenesulfonic acid [9], fluorine acids [10,11] and Lewis acids [12–17] are used. Condensation of aniline with carbonyl compounds is also possible to perform in the presence of heterogeneous catalysts. It should be noted, however, that this issue has not been particularly more deeply examined, particularly with regard to the analysis of reaction selectivity, which is reflected in the relatively small number of reports on the subject. Shaikh described the study on condensation of aniline with carbonyl compounds with the use of various special catalysts with mesoporous structure, prepared in the reaction of thionyl chloride and mesoporous silicate [18]. At temperature of 80 °C, in the presence of toluene as a solvent, he obtained corresponding quinoline derivatives with the yields of 57 ÷ 62 wt%. Sidhe used the same catalyst in the reaction of acetylaniline with various ketones [19]. The yields of corresponding quinolines were from 50 to 80 wt%. In turn, Venkateswarlu as catalyst used Chloramine-T [20]. In the presence of acetonitrile as a solvent, in temperature of 80 °C, the yield of quinoline derivatives was 95 wt%. High yields of quinoline derivatives have been achieved in the reaction catalysed by heteropolyacids. Heravi in Friedlander modification of Skraup method (80 °C, 3 ÷ 5 h) obtained quinolines with the yield of 91 wt% [21]. Heteropolyacids, in particular phosphomolybdic acid, were used as catalysts in the study conducted by Chaskar [22].

Studies described above concerned very particular cases of

\* Corresponding author.

E-mail address: [nowicki.j@icso.com.pl](mailto:nowicki.j@icso.com.pl) (J. Nowicki).



**Scheme 1.** Synthesis pathway of 2,2,4-trimethyl-1,2-*H*-dihydroquinoline (TMQ) according to Skraup mechanism.

condensation of aniline with various carbonyl compounds leading to corresponding quinoline derivatives. Among of the described results, only a few of them describe the synthesis of 2,2,4-trimethyl-1,2-*H*-dihydroquinoline. Yadav described the synthesis of TMQ in the reaction of aniline with acetone in the presence of catalyst based on sesquioxane framework, functionalized by acidic sulfonic group [23]. At temperature of 80 °C he achieved quinoline with the yield of 90 wt%. Hegedüs used as catalyst klinoptilolite modified by sulfuric acid [24]. The reaction of aniline with acetone was conducted in temperature of 110 °C in the presence of toluene as a solvent. The amount of used catalyst was, however, very significant *i.e.* 4.3 g/g aniline. In above reaction conditions TMQ was achieved with the yield of 95 wt%. Methyl analog of TMQ was obtained in the reaction of 3-methylaniline with acetone in the presence of Amberlyst A15 as a catalyst [25]. The yield of MeTMQ was very high (93 wt%) but after long time of synthesis (48 h).

TMQ is considered as commercial product of great practical importance, but in none of the abovementioned papers on the synthesis of TMQ, did not provide more detailed information about characteristic of the post-synthesis mixture. These informations are useful for the assessment of the course of this very complex synthesis, especially the selectivity of the reaction of aniline with acetone catalysed by heterogeneous catalysts.

Owing to the relevance of TMQ and also its methyl analogues, we described the novel approach to the synthesis of important 1,2-DHQ derivatives with the use of selected sulfonic acid silica catalysts. The detailed structural analysis of reaction products have been presented for the first time.

## 2. Experimental

### 2.1. Materials

Aniline for synth. (99%), acetone puriss. p.a. (> 99.5%) and mesityl oxide for synth. were supplied by Aldrich (Poland). SBA-15 silicas were synthesized using a hydrothermal procedure. As the precursors were used: tetraethylorthosilicate (TEOS, 98%) supplied by Aldrich (Poland) as a silica source, nonionic triblock co-polymer Pluronic P123 [poly(ethylene oxide)-block-(poly(propylene oxide))-block-poly(ethylene oxide)], molecular weight = 5800, supplied by Aldrich (Poland) as a template, chlorotrimethylsilane puriss. (CTMS, 99%), phenyltriethoxysilane (PTES) for synth. and chlorosulfonic acid supplied by Aldrich (Poland) as functional modifiers. Distilled water, hydrochloric acid and dichloromethane puriss. p.a. were supplied by POCh (Poland).

### 2.2. Catalysts preparation

Mesoporous molecular sieves of SBA-15 were synthesized according to the method described in the literature with some modifications [26,27]. In a typical synthesis, P123 (4 g) was dissolved in an aqueous solution of HCl (1.6 M HCl, 150 g) at a room temperature, under vigorous stirring. Subsequently, a 8.5 g of TEOS was added to the above

solution. The molar composition of the reactants used in these synthesis was 1 SiO<sub>2</sub>: 0.017 Pluronic P123: 5.88 HCl:192 H<sub>2</sub>O. After stirring at 40 °C for 2 h, the reaction mixture was transferred into a Teflon bottle and aged at 100 °C for 48 h under static conditions. The mixture was then allowed to cool to room temperature, and the solid, white product was filtered, dried at 110 °C for 12 h and calcined at 550 °C for 8 h (temperature gradient 5 °C/min). Typical yield of pure SBA-15 was 96 wt% based on used SiO<sub>2</sub>.

For the synthesis of organosulfonic acid functionalized silicas was applied post-synthesis method based on the work described by Mrowiec-Białoń (SBA-15) [28] and Karimi (SiO<sub>2</sub>) [29]. First, pure siliceous materials (SBA-15) were contacted with water steam for 2.5 h and subsequently calcined at 200 °C for 2 h. The nominal content of organic groups was 1.0 mmol g<sup>-1</sup>. All the operations were made under a nitrogen atmosphere. The synthesis pathway of the preparation of organosulfonic acid functionalized SBA-15 is presented in Fig. 1.

In a preparation of the SBA-15-*propyl-SO<sub>3</sub>H* catalyst, a mixture of corresponding silica and MPTMS in *n*-hexane was magnetically stirred for 15 min at room temperature, and then refluxed for 24 h at 45 °C (Fig. 1a); all the above operations were made under a nitrogen atmosphere. Then the reaction mixture was cooled, and the solvent was removed by evaporation and the product was dried at 60 °C for 24 h. After that mercaptopropyl groups were oxidized with 30% aqueous hydrogen peroxide solution under stirring at 40 °C for 24 h under nitrogen atmosphere. After filtration, the solid product was washed with deionized water. The material was filtered and washed several times with water and ethanol. The wet material (1.0 wt%) was suspended in 1 M H<sub>2</sub>SO<sub>4</sub> for 2 h. Finally the material was filtered, washed with water and ethanol, dried at 60 °C under vacuum overnight. The catalysts were denoted as SBA-15-*Pr-SO<sub>3</sub>H*. Using amorphous silicas in the place of SBA-15 corresponding organosulfonic acid modified silica catalysts were obtained and denoted as SiO<sub>2</sub>-*Pr-SO<sub>3</sub>H*.

The SBA-15-*phenyl-SO<sub>3</sub>H* catalyst were prepared by grafting of PTES over the silicas (Fig. 1b). The calcined SBA-15 material was refluxed with excess quantity of PTES dissolved in *n*-hexane under nitrogen atmosphere overnight for 24 h at 45 °C. Then the reaction mixture was cooled, then the solvent was removed by evaporation and the product was dried at 60 °C for 24 h. The obtained material further reacted with chlorosulfonic acid, which resulted in generating the phenyl sulfonic acid groups. The material was degassed at 130 °C under vacuum for 12 h and then 30 mL of CH<sub>2</sub>Cl<sub>2</sub> containing chlorosulfonic acid (1 mL) was slowly added at room temperature under nitrogen atmosphere. After 4 h of stirring, the suspension was slowly added to the mixture of water and ice (0 °C). After filtration, the solid product was washed with deionized water. Finally the powder product was dried at 60 °C under vacuum overnight. To improve the hydrophobicity of the catalyst's surface, methyl groups (nominal content of methyl groups was 1 mmol g<sup>-1</sup>) were introduced by grafting chlorotrimethylsilane (CTMS). The catalyst was denoted as SBA-15-*Ph-SO<sub>3</sub>H*(-CH<sub>3</sub>) (Fig. 1c).

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