



## Investigated on the Rubber Antioxidant 2,2,4-Trimethyl-1,2-dihydroquinoline Polymer

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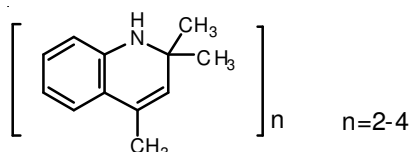
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The paper investigated the mechanism of the reaction which are used in synthesis of 2,2,4-trimethyl-1,2-dihydroquinoline and 2,2,4-trimethyl-1,2-dihydroquinoline polymer. Aromatic amines and  $\alpha$ -alkenyl alkyl ether condensation of synthetic quinoline and polymerization. one is acetone, aniline on direct condensation to form Schiff base and then further reduced synthesis loop; the other is the first for two molecules of acetone condensation to form *iso*-propylidene acetone and then *iso*-propylidene acetone condense with aniline ring. Aniline and acryldehyde will not form Schiff base in acid and directed formed quinoline. Acetone molecules to produce diacetone alcohol, diacetone alcohol shrink generated *iso*-propylidene acetone. In acidic conditions, *iso*-propylidene acetone oxygen atoms combine to form hydroxyl and hydrogen ions to form positively charged enol structure. Others aniline and acetone, carried out the nucleophilic addition reaction of N-isopropyl aniline fork. Two molecules of N-isopropyl fork intermediates after addition of aniline, cyclization under acidic conditions, off part of aniline to produce a monomer of 2,2,4-trimethyl-1,2-dihydroquinoline.

**Key Words:** Synthesis, 2,2,4-Trimethyl-1,2-dihydroquinoline.

### INTRODUCTION

Rubber antioxidant (RD) (2,2,4-trimethyl-1,2-dihydroquinoline polymer)<sup>1,2</sup>,  $(C_{12}H_{15}N)_n$ ,  $n = 2-4$ ) is a ketone amine antioxidant.



It performs excellently on the protection of oxidation of rubber which is caused by thermal oxidative aging and catalytic oxidation by metal ions. Rubber antioxidant is mainly used for natural rubber and chloroprene rubber *etc.* It has excellent effects to the ageing caused by heating and oxygen and has stronger restrained effect to the metallic catalysis and oxidation, it is suitable for natural, buna-s, buna-N and chloroprene rubbers. Rubber antioxidant RD has a longer-time remaining of protective effect, because it has a higher molecular weight and has little diffusive loss. So it is suitable for the rubber products used in tropical area.

Antioxidant RD production process is not complicated, polymerized only by ordinary materials, but the product contains components of different degree of polymerization of the polymer content of polymer, the proportion of affected

more product's performance, which constitutes the special nature of the product, complexity. Thus from the antioxidant RD has since the date of the birth of a new technology for the improvement or to optimize performance, or increase yield, or improved technology, *etc.* Antioxidant RD is a variety of polymers as a mixture, which is the active ingredient of which, how best to generate it has become one of the most concerned about. These are related to the reaction mechanism problems, which have been someone conduct a study and explore.

Now widely recognized that the synthesis of antioxidant RD process involves large stages: first, condensation of aniline with acetone monomer 2,2,4-trimethyl-1,2-dihydroquinoline process; followed by the monomer in the acid-catalyzed the polymerization process. Generated from the monomer during the preparation of the aniline substituent with a monomer structure, in which the aniline molecule may also continue to generate another monomer with acetone condensation to form dimers. Typically, the condensation reaction is slow, but faster polymerization. Therefore, the product obtained is a mixture rather than the pure monomer.

Now widely recognized that the synthesis of antioxidant RD process involves two stages: first, condensation of aniline with acetone monomer 2,2,4-trimethyl-1,2-dihydroquinoline process; followed by the monomer in the acid-catalyzed the polymerization process. Generated from the monomer during

the preparation of the aniline substituent with a monomer structure, in which the aniline molecule may also continue to generate another monomer with acetone condensation to form dimers. Typically, the condensation reaction is slow, but faster polymerization. Therefore, the product obtained is a mixture rather than the pure monomer<sup>3,4</sup>.

The formation of monomer involves two possible mechanistic model: one is acetone, aniline direct condensation to form Schiff base and then further reduced synthesis loop and the other is the first for two molecules of acetone condensation to form *iso*-propylidene acetone and then *iso*-propylidene acetone condense with aniline ring.

Institute of Organic Chemical the former Soviet Union made aromatic amines are reacted with isopropenyl alkyl ethers condensation of synthetic quinoline compounds into the ring after a Schiff base reaction mechanism<sup>5</sup>. Isopropenyl ethyl ether is preferable employed as the isopropenyl alkyl ether<sup>6</sup>. First of aromatic ether amine addition to unsaturated double bond, the formation of unstable intermediates and then lose a molecule alcohols, ketones amine condensate obtained Schiff base. Schiff base and then with the second unsaturated ether molecules diene addition reaction, the formation of unstable 4-alkoxy-tetrahydroquinoline intermediates. The latter under the reaction conditions off an alcohol molecule to form the final product of 1,2 twelve hydrogenated quinoline derivatives. Reaction is exothermic, the  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  or aluminum bromide,  $\text{AlBr}_3$  is preferably used as the catalyst<sup>6</sup> in the presence of the reaction rate is also faster, so the need to control the temperature does not exceed 50 °C. In the synthesis of antioxidant RD acidic conditions, the acetone oxygen atom can be protonated to get a enol tautomer and with the keto tautomer to achieve balance (Figs. 1 and 2).

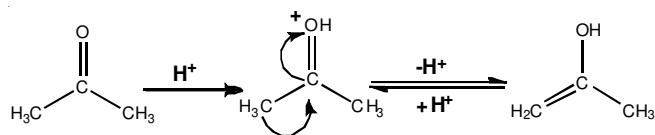


Fig. 1. Acetone get an enol tautomer

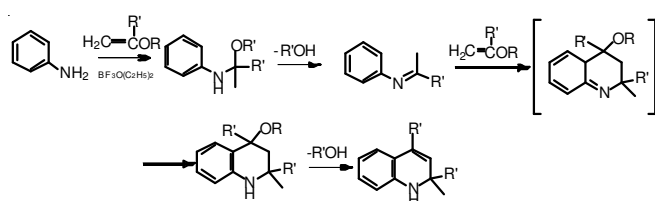


Fig. 2. Aromatic amines and  $\alpha$ -alkenyl alkyl ether condensation of synthetic quinoline compounds into the ring after a Schiff base reaction mechanism

As above, aniline and enol tautomer Schiff base reaction and further reaction of enol tautomer is generated monomer. But this lack of direct evidence. Ketones, aromatic amines to form Schiff base with the acid is very harsh conditions, general requirements pH of *ca.* 4.5, when the reaction medium pH is too low or too high, the resulting Schiff base rate is very slow. Condensation of aniline with acetone usually carried out under strongly acidic conditions, when the aniline protonated nitrogen atoms are also serious, is not conducive to generating

amine tetrahedral intermediate, while the acetone condensation is more appropriate.

Acheson also believe that the acid in the Skraup reaction conditions, aniline and acrolein will not form Schiff base, that is, according to reaction line Shown in Fig. 3.

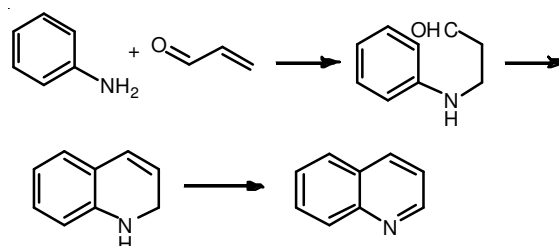


Fig. 3. Aniline and acrolein reaction mechanism

When iodine, *p*-toluene sulfonic acid as the catalyst, whether or ethoxy aniline or aniline condensation with butyraldehyde have had more time Schiff base, distillation and then recycled to the system applied to the reaction process was the purpose of the product. When using acetone, methyl ethyl ketone, methyl isobutyl ketone, when there are no special instructions Schiff base formation.

In the Skraup reaction, if one uses a 2-butene formaldehyde, methyl vinyl ketone instead of acrolein and aniline, respectively, will form the corresponding 2-methyl-quinoline and 4-methyl-quinoline, shows the position of methyl aniline in the reaction with amino-allyl bond in the first  $\beta$ -carbon atom reactions or methyl position to change. In the Doebner-Miller reaction, the first acetal synthesis of 2-butene-formaldehyde and then the reaction of quinoline with aniline. Reaction to form *N*-ethyl aniline and *N*-butyl-aniline-products. This indicates that part of the condensation of aniline with acetaldehyde Schiff base formation, which then formed dihydroquinoline dehydrogenation get quinoline, shown in Fig. 4. If acetaldehyde into acetone, the formation of 2,2,4-trimethyl-1,2-dihydroquinoline, rather than the 2,2,4-trimethyl-quinoline, which is another example of the synthesis of single-the process of the body did not form Schiff base.

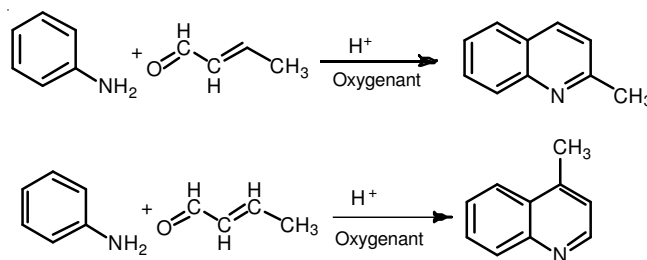


Fig. 4. (E)-But-2-enal and aniline reaction mechanism

When the aldehyde as raw material are susceptible to the formation of Schiff base and with the ketone as raw materials difficult to form the Schiff base. Thus condensation of aniline with acetone monomer process is: under acidic conditions, Aldol condensation of two acetone molecules to produce diacetone alcohol, diacetone alcohol shrink generated *iso*-propylidene acetone. In acidic conditions, isopropylidene acetone oxygen atoms combine to form hydroxyl and hydrogen ions to form positively charged enol structure. Aniline lone

pair of electrons with the nitrogen atom attack isopropylidene acetone positively charged  $\beta$ -carbon atom, forming NC bond and then dehydroxylation is hydrogen ions combine to form carbonium ions, carbonium ions derived from ortho attack on the benzene ring, the closed-loop after the formation of 2,2,4-trimethyl-1,2-dihydroquinoline monomer, which is typical of Doebner-Miller variant (Doebner-Miller quinoline synthesis reaction of the compounds belonging to the classical Skraup reaction variants). In addition to aniline, isopropylidene acetone (or diacetone alcohol) in acidic conditions, such as raw materials can be synthesized under the same antioxidant RD, which explains the mechanism through isopropylidene acetone reasonable<sup>7</sup>, shown in Fig. 5.

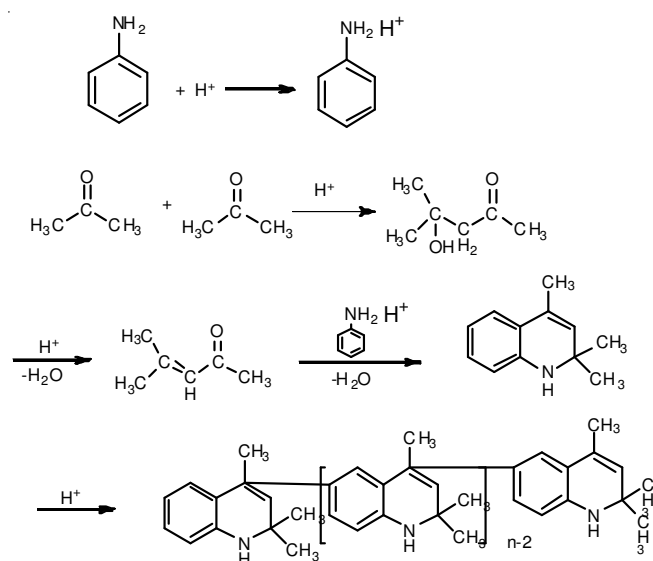


Fig. 5. Aniline and acetone reaction mechanism

And  $\text{D}_2\text{O}$  isotope labeled according to NMR analysis, 3,4-bit C atoms of hydrogen, alkyl is more easily replaced, which is more easy to form  $\text{C}^+$  and the alignment of amino monomer in the adjacent bit more lively, by  $\text{C}^+$ , electrophilic attack to form C-C bond, has been linked dimer 4,6-position. After several times of the aromatic electrophilic substitution reaction that produces polymer compounds. The right care can be compared with two molecules of aniline condensation of acetaldehyde with Doebner-Miller synthesis, aniline and a member of a member of acetaldehyde and acetone condensation of Ber synthesis, aniline condensation of acetone with two molecules of Riehm synthesis and with the traditional Skraup comparison method for ketone synthesis that condensation of aniline with two molecules of acetone when acetone condensation before a, *p*-unsaturated ketone and then with aniline by 1,4-addition of Michael addition manner, the last generation quinoline derivatives.

Others aniline and acetone, carried out the nucleophilic addition reaction of N-isopropyl aniline fork. Two molecules of N-isopropyl fork intermediates after addition of aniline, cyclization under acidic conditions, off part of aniline to produce a monomer of 2,2,4-trimethyl-1,2-dihydroquinoline, shown in Fig. 6.

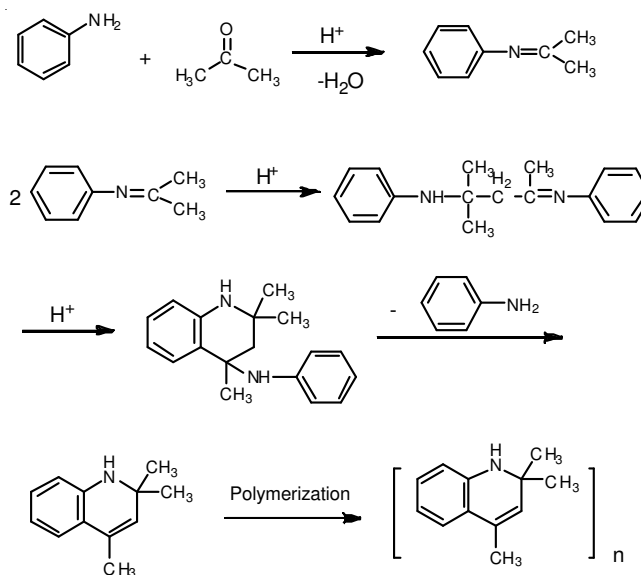


Fig. 6. Aniline and acetone reaction mechanism

In summary, the synthesis of antioxidant RD in the presence of multiple parallel reactions and a series of reaction, the reaction of the complexity of the product composition of complexity. From the apparent point of view, the formation of monomer and polymerization reaction is the dominant reaction of many. Integration of experimental results can be obtained, aniline, acetone condensation reaction mechanism is antioxidant RD: First of all should be two molecules of acetone condensation to form *iso*-propylidene acetone and then condensation of aniline and the formation of monomer, the final monomer polymerization end products, shown in Fig. 5. Content of impurities and analysis to help find ways to improve antioxidant RD quality measures. These efforts often involve a number of high-tech, high-end equipment use and high costs, although some companies do some work, but not enough, therefore, should pay attention to this work, to further improve our level of production technology antioxidant RD for the rubber industry.

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