

Clean and facile synthesis of triuret from urea and dimethyl carbonate (DMC) under mild conditions

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Abstract—Triuret has been successfully synthesized by the reaction of urea with dimethyl carbonate (DMC) under mild conditions in the presence of potassium methoxide as a catalyst. It has been fully characterized by FT-IR, ¹H-NMR, ¹³C-NMR, and MS. Effects of the catalyst, the molar ratio of starting materials, and the reaction time on the obtained product were examined in detail. It was found that when *n* (urea) : *n* (DMC) = 1.2 : 1, 6 h, and 0.8% catalyst, the yield of triuret can reach 98.1%. Especially, this novel procedure is reported for the first time and has many significant advantages such as easy and clean synthesis, simple work up, and high yields.

Key words: Triuret, Dimethyl Carbonate, Urea, Clean Synthesis

INTRODUCTION

Triuret (also known as carbonyldiurea, dicarbonyl-urea, or 2,4-diimidotricarbonic diamide) is a nitrogen-rich compound that can be regarded as one of the most concentrated forms of peptide bonds. It has been confirmed as a control-released fertilizer without negative environmental effects because of its less solubility and better structure than urea. Furthermore, its effectiveness has been qualitatively demonstrated [1-3]. Triuret, a by-product of purine degradation in living organisms, has been considered as a significant agent with potential biochemical and physiological significance [4,5].

Triuret, a product of amide-forming condensation reaction, has drawn considerable attention worldwide. Many reports are available on the synthesis of triuret, including direct heating urea in inertia solvent, reaction of urea with phosgene, or treatment of ammonia with carbonated diisocyanate [6-8]. However, the reported methodologies have some drawbacks, such as low yields, lack of availability, tedious synthetic process, or use of toxic organic solvents.

In this paper, we report a facile and clean synthesis of triuret from urea and dimethyl carbonate (DMC) in the presence of potassium methoxide under mild conditions, which can be considered as the ammonolysis reaction of DMC. Moreover, the only by-product methanol could directly react with CO₂ to reproduce DMC as reported, by which we may achieve reaction recycling. This novel procedure is expected to be applied on industrial application research.

MATERIALS AND METHODS

1. Materials

Urea, dimethylcarbonate (DMC), potassium methoxide and methanol were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. These raw materials were all of analytical reagent grade

and used without further purification.

2. Synthesis of Triuret

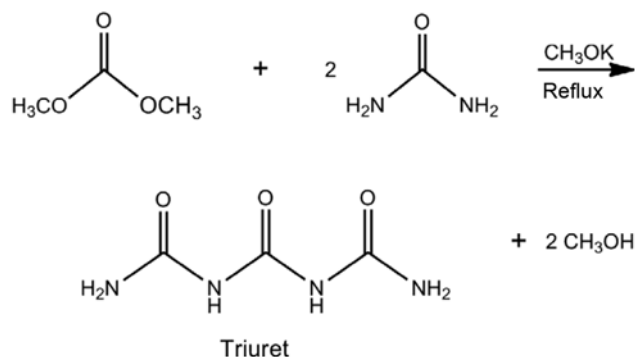
As shown in Scheme 1, a mixture of DMC (0.5 mol) and urea (0.6 mol) with potassium methoxide (0.004 mol, 1 mol% of urea) as a catalyst was stirred and refluxed for 5 h, and then the reaction mixture was distilled for additional 1 h to remove the methanol. After reaction, the resultant product was cooled and filtered. The filtrate was washed with methanol three times and then dried to afford triuret as a white solid in 98.1% yield.

Triuret: a white solid, yield 98.1%. IR (KBr disk) ν/cm^{-1} : 3453, 3351, 3267, 2965, 1740, 1581, 1522, 1457, 1402, 1227, 1106; ¹H-NMR (*d*₆-DMSO) δ/ppm : 9.91 (s, -CO-NH-CO-, 2H), 7.16, 7.27 (2s, CCO-NH₂, 4H); ¹³C-NMR (*d*₆-DMSO) δ/ppm : 150.43 (-CO-NH-), 155.96 (-CO-NH₂); MS (*m/z*): 61, 87, 104, 130, 146 (*M*+H)⁺.

RESULTS AND DISCUSSION

1. The Synthesis of Triuret

The synthesis of triuret is shown in Scheme 1. The raw material DMC, which was known as eco-friendly agent, is hardly poisonous and has little negative repercussions to human beings as well



Scheme 1. Synthetic route of triuret.

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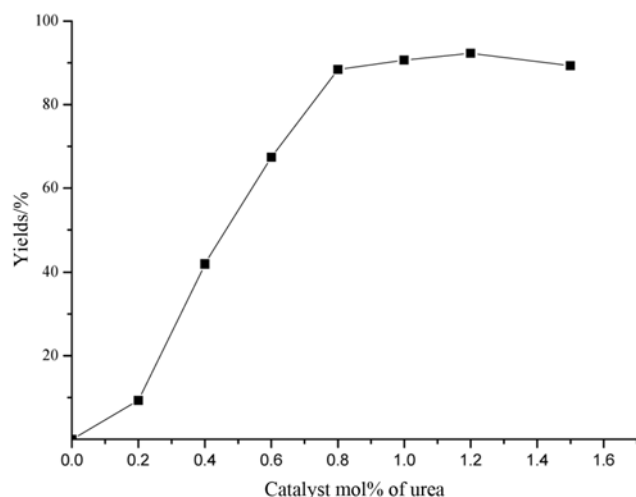


Fig. 1. Effect of the quantity of catalyst on the yields with $n(\text{urea}) : n(\text{DMC})=2.0 : 1$, 4 h and reflux.

as the environment. The product triuret was synthesized from DMC and urea under mild conditions with methanol as by-product. Especially, methanol can directly react with CO_2 to reproduce DMC according to the reports in the literature [9-13], by which synthetic process could achieve one recycling. The aforementioned recycle indirectly realize the chemical fixation of CO_2 by urea. In addition, the yield of triuret was 98.1% under the optimized conditions, which was at least 25% higher than those of traditional methods [8,14].

2. Influence of the Quantity of Catalyst on Yields of Triuret

Influence of the amount of catalyst on yields of triuret presented in Fig. 1. It is clear that the yield increases from 0.2% to 1.2% and then decreases with a further increase in the quantity of CH_3OK . This behavior may be interpreted in terms that a higher concentration of methoxy group increases the electronic density of nitrogen atoms by attacking hydrogen atom of amino-group. In a certain range of catalyst dosage, the concentration of the activated urea increases with the increase of potassium methoxide, resulting in the increase of yield. However, when the amount of catalyst is above 1.2%, the excessive methoxy ions would reduce the reactivity of the activated urea for the increase of solution polarity, thus resulting in the decrease of the yields.

As shown in Fig. 1, the yield of triuret was 88.4% when the content of catalyst was 0.8%. However, the maximum yield of triuret was 92.3% when the content of CH_3OK was above 1.2%. Although the additional 0.4% catalyst increased another 3.9% triuret, it would significantly increase production cost because potassium methoxide is much more expensive than triuret. Consequently, the optimized catalyst content may be 0.8% from the perspective of lower cost.

3. The Influence of $n(\text{urea}) : n(\text{DMC})$ on the Yields of Triuret

As shown in Fig. 2, the yield of triuret gradually increases when the range of the molar ratio of DMC to urea is from 1 : 1.0 to 1 : 1.8, but decreases sharply when that of DMC to urea is 1 : 2.0. Initially, we investigated the ammonolysis reaction of DMC with urea at $n(\text{DMC}) : n(\text{urea})=1 : 2.0$ which was consistent with the theoretical calculating value. However, the yield of triuret was about 62% re-

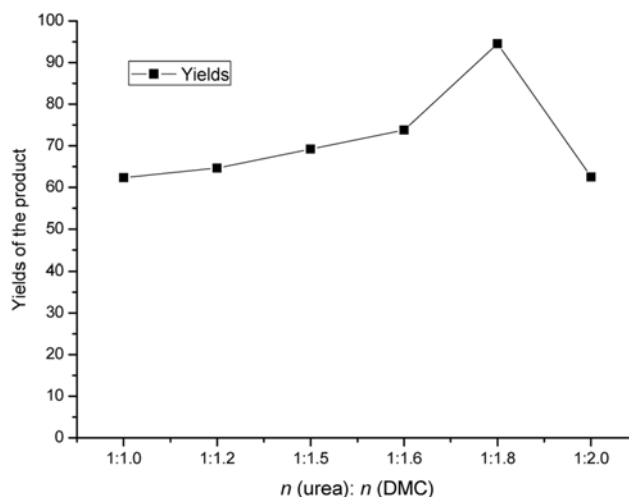
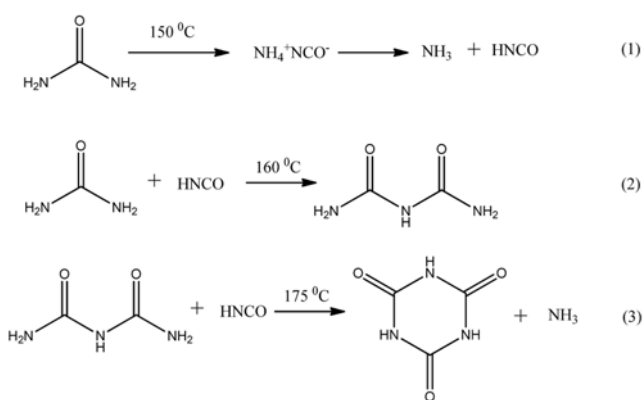


Fig. 2. The influence of $n(\text{urea}) : n(\text{DMC})$ on the yields of triuret. The synthesis conditions: CH_3OK , 0.8 mol% of urea; reaction time=4 h; reflux.



Scheme 2. The side-reaction of urea above the melting point of urea.

gardless of the change of catalyst amount and reaction time. This is because the by-product of methanol distilled together with DMC in form of the azeotropic mixture, which may lead to the decrease in the amount of DMC participating in the reaction. Thus, excess amount of DMC should be added in order to raise the yield of triuret.

It is recently reported that the yield of triuret generated from urea by heating above the melt point is much lower because it is mostly converted to biuret and cyanuric acid by the traditional methods [15-17]. The detailed description on the side reactions mechanism related to the traditional methods is shown in Scheme 2. Urea begins to form ammonium cyanate first at 152 °C, and then decomposes into ammonium and cyanic acid. HNCO , as the product of urea decomposition, begins to react with intact urea to produce biuret at approximately 160 °C. With the increase of the reaction temperature, a small amount of HNCO can further react with biuret to form cyanuric acid. Consequently, the high yield of triuret obtained in our study can be due to the few side reactions under the mild conditions.

4. The Influence of Reaction Time on the Yields of Triuret

Further studies of the influence of reaction time on yield of triuret were initially conducted with $n(\text{DMC}) : n(\text{urea})=1 : 1.8$ as well as in the range of reaction time from 5 to 7 h, but it was found that

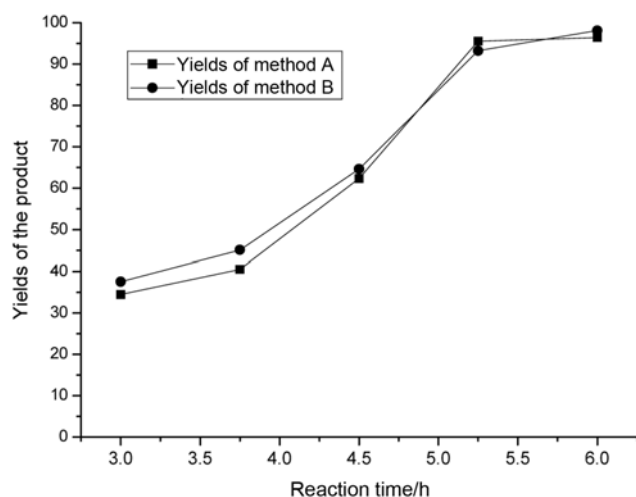


Fig. 3. The influence of reaction time on the yields of triuret. Synthesis conditions of method A: $n(\text{DMC}) : n(\text{urea}) = 1 : 1.0$; CH_3OK , 0.8 mol% of urea; reflux. Synthesis conditions of method B: $n(\text{DMC}) : n(\text{urea}) = 1 : 1.2$; CH_3OK , 0.8 mol% of urea; reflux.

the yield of triuret has no significant change compared to that of the same reaction time with 4 h. Consequently, the following studies on the effect of reaction time were performed using method A and method B. As shown in Fig. 3, the yield of triuret clearly rises with the increase of the reaction time ranging from 3 to 6 h, which may be ascribed to the chemical equilibrium. Obviously, in the presence of the different molar ratio of DMC to urea, the yield of triuret for method B is always higher than that of triuret for method A under the same reaction conditions, which may result from the inadequate addition of the urea in the reaction of Method A. Furthermore, it can be seen from the yields of triuret at different reaction time that the product triuret cannot continue to react with DMC.

In addition, the ammonolysis reaction of DMC with urea is gradually achieved and only triuret is produced because the product cannot further react with DMC or urea to form hexuret, nonuret and undiciuret, etc., as time goes on. As a result, the appropriate elongation of the reaction time can assist to increase the yield of triuret that is the only product under the mild reaction conditions.

CONCLUSIONS

This is the first report that triuret was simply synthesized from urea and DMC under mild conditions. The yield of triuret was 98.1% at the optimized conditions of $n(\text{DMC}) : n(\text{urea}) = 1 : 1.2$, and 0.8

mol% potassium methoxide (the molar ratio of urea) with reaction time of 6 h. It is noteworthy that we have developed a practical, efficient, and convenient ammonolysis procedure for converting urea to triuret with potassium methoxide as a catalyst. This procedure offers significant advantages over the earlier reported methods because the present route is characteristic of short reaction time, simple reaction procedure, high yield, and mild conditions.

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