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Preparation of Triacetoneamine, an Improved Method

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PREPARATION OF TRIACETONEAMINE, AN IMPROVED METHOD

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Abstract: A new method for the preparation of triacetoneamine has been developed, in which, p–nitrotoluene is used as a catalyst, the yeild of triacetoneamine is up to 65%

Triacetoneamine, 4–oxo–2, 2, 6, 6–tetramethylpiperidine, is an important compound since it represents key intermediate in the preparation of the stable nitroxyl radical such as 4–hydroxy–2, 2, 6, 6– tetramethylpiperidine – 1– oxyl and 4– amino– 2, 2, 6, 6– tetramethylpiperidine– 1– oxyl, which are used in spin– labing medicine′s studies [5] and as a new efficient photostablizing agents for plastic products [6] .

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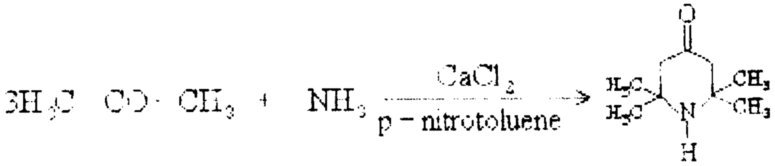
In the past years, several methods have been developed for the preparation of triacetoneamine.It can be obtained from phorone and ammonia[7], or from acetonin (2, 2, 4, 4, 6–pentamethyl–2, 3, 4, 5–tetrahydropyrimidine) and acetone, in the presence of catalyst.Of all the methods in literature, the simplest and most frequently used one remains the condensation of acetone with ammonia in the presence of calcium chloride[9–14]

However, the yield of triacetoneamine, up to now, is still low even for the best method mentioned above, varys only from 8 to 32%, and in some cases rather elaborate equipments are involved, the reaction has to last seven days or more[15]

Here, we have deveIeped a new method for the preparation of triacetoneamine, in which, p–nitrotoluene is used as a catalyst, triacetoneamine is obtained in high yield from acetone, ammonia and calcuim chloride.



The yield, taking into account of the recovered acetone, is up to 65% and no elaborate equipments are used, the reaction won't take long time.

In our works, the various effects such as temparature, rate of stirring, amount of ammonia, partical size of calcium chloride and acid catalysts are studied .The result obtained shows that only efficient route for increasing the yield is to select catalysts.Then, in order to explore efficient catalysts, many compounds are investigated, these compounds include inorganic substance such as nitrate, halide and sulfate of Fe, Sn, Ca, Mg, Mn, Co, Ni, Pb, Cr, Na, K, Al, Cu, Ti, and some rare earth oxides such as La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O, Td_2O_3, Ho_2O_3, Tm_2O_3, $Yb_2O_3$and Lu_2O_3. But , to our dispointed, these all materials, are found to have no remarkable catalytic activity to the reaction.

At last, in our works, the catalytic activity of some organic compounds are studied . According to our privous studies, we regard the nitrogenous compounds as the main screened materials, the following nitrogenous compounds are tested: 2–nitropyridine, p– nitrophenol, o– nitrophenol, 1– nitronaphthalene, p– nitroethylbenzene, nitromethane, p– nitrotoluene, 2, 4, 6– trinitrophenol. Of all the compounds, we find that only p–nitrotoluene shows efficient catalytic activity in the synthetic reaction of triacetoneamine, the rest have weak action or not.

Experimental

In a 2. 5L round– bottom three– necked flask equipped with heavy duty stirrer, condensor and cool water bath, 4– 20 mesh anhydrous calcium (2000ml) , chloride (600g) , commercial acetone, ammonium chloride (60g) and p–nitrotoluene (1–2g) were placed. Anhydrous ammonia was introduced continually by bubble through the stirred mixture for 12–15hr at 25–30℃ .As the resulting mixture converted into liquid state, stoped stirring. After standed for 1–2hr, the liquid was stratified.The upper strata of yellow organic solution was isolated, the remained aqueous slurry was extracted with diethyl ether (3 × 500ml) .The combined oil and extract weighed a total of 1300g.

In a 2L round–bottom three–necked flask, the aforementioned products, 4–20 mesh anhydrous calcium chloride (550g), acetone (320ml) and water (400ml) were introduced, the resulting mixture was stirred for 24hr at 45–50℃ and then cooled to room temperature. It was basificated with 25% NaOH, and extracted with diethy ether (3 × 700ml) .The extract was dried with $MgSO_4$and then distilled under reduced pressure to give 650g triacetoneamine, yield, 65% (taking into account of the recovered acetone) .b.p.95–100℃ / 700Pa; MS (EI), m / z: 155 ($M^{\dot{+}}$), 140, 139, 111, 98.

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