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NOTE

1,2,3-Trione Compounds Synthesis by Oxidation 1,3-Diketones

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For synthesis of the 1,2,3-trione compounds from 1,3-diketones was utilized SeO_2-H_2O_2 as oxidative agents and T.H.F.-H_2O as solvent. This method has better yield in comparison with the similar methods.

Key Words: Oxidation, 1,3-Diketones, 1,2,3-Triones, Selenium oxide, Hydrogen peroxide.

The synthesis of 1,2,3-triones can be achieved from 1,3-diketones by oxidation with selenium dioxide (SeO_2) in a suitable solvent. There are some methods for synthesis of these compounds[1,2]. Some of the selenium dioxide uses are: analysis (testing for alkaloides, oxidizing agent, antioxidant in lubricating oils and catalyst[3]. The synthesis of **2** from compound **1** was reported with SeO_2/1,4-dioxane[4]. One of the synthesis methods for producing **4** is oxidation of uric acid by using $KClO_3$/HCl and H_2S addition to the first step product. The other method is addition HNO_3 and then H_2S to 1,3-diones for producing 1,2,3-triones. Compound **4** was synthesized from alloxantine in presence of nitric acid. The oxidation reaction of **3** in two steps produced **4**. The condensation between **3** and benzaldehyde was occurred and then oxidation the product of the first step by using CrO_3 produced **4**[1,2]. Oxidation of barbituric acid (**3**) by SeO_2 in 1,4-dioxane was not succesful[5]. In this study, the oxidation some of the 1,3-diketones (**1,3,5**) to 1,2,3-triones (**2,4,6**) is reported by changing the solvent system to THF-H_2O and utilize SeO_2-H_2O_2 as oxidative agents[5].

Some of these compounds are very useful materials in chemistry and chemical industry. Ninhydrin (**2**) is used as chemical intermediate, reagent for determination of amines, amino acids and ascorbic acid. Alloxane (**4**) is one of the materials in organic and bioorganic synthesis, biochemical research, pharmaceutical industry, foodstuff and applied as an antitumor precursor compounds. Similar to **2** and **4** could use from compound **6** in condensation reactions and related organic compounds synthesis[4-6].

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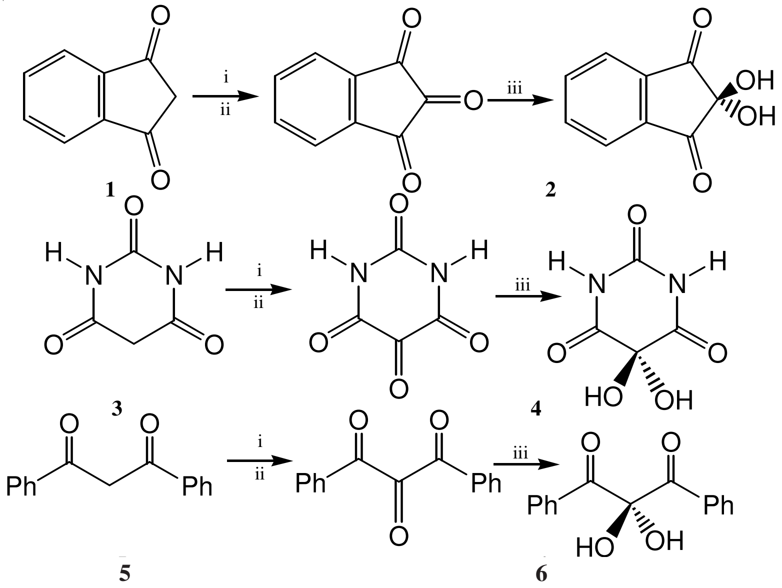

i = SeO_2-H_2O_2; ii = THF-H_2O; iii = H_2O

The compounds **2**, **4** and **6** were synthesized here, are known compounds and those physical data, FT-IR and ^{1}H NMR spectra were essentially identical with those authentic samples[3,7]. The FT-IR spectra was recorded as KBr pellets on a Shimadzu FT-IR 8000 spectrometer. ^{1}H NMR spectra was determined on a 300 MHz Brüker spectrometer (Table-1).

TABLE-1
SELECTED DATA OF **2**, **4** AND **6** (FT-IR IN cm^{-1}, ^{1}H NMR IN ppm AND MELTING POINT IN °C. ALL SOLVENTS IN ^{1}H NMR WAS D_2O)

No. of compds.	Data	Yield (%)
2	m.p. = 240-245 FT-IR: 3300 (O-H, st.); 3050, 3150 (Ar_{C-H}); 1723, 1753 (C=O); 1460, 1600 ($Ar_{C=C}$); 1060, 1150 (C-O). ^{1}H NMR: 7.5 (4H, s, A_4 sys.).	48
4	m.p. = 168-170 FT-IR: 3452 (O-H, st.); 3298 (N-H, st); 3050, 3150 (Ar_{C-H}); 1745, 1704, 1680 (C=O); 1050, 1150 (C-O). ^{1}H NMR: 6.8-7.2 (t, 1:1:1, 2H, NH).	50
6	m.p. = 220-222 (deg.) 43% FT-IR: 3350 (O-H, st.); 3075, 3166 (Ar_{C-H}); 1710, 1700 (C=O); 1477, 1600 ($Ar_{C=C}$); 1060, 1175 (C-O). ^{1}H NMR: 7.60 (10H, s, Ar, m.).	43

Typical procedure: In a 250 mL three necked flask, fitted with a reflux condenser and stirrer, place 2.25 g dissolved in 60 mL T.H.F. and 10 mL H_2O_2 (34 %). Hold the stirred solution in 30-40ºC, until to produce a pellucid solution. Then cooled the mixture under 10ºC. Add 6.4 g of crude barbituric acid (**3**) (1,3-diketones **1**, **3** and **5**) must add in small quantities). Reflux the resulting mixture for 5 h in 60ºC. A white solid separates during the reflux period. Filter the mixture, transfer the filtrate to a rotary evaporator apparatus and distill it about 45 mL of solvent. Then add 25 mL of distilled water and boil the solution. For removing the solid residue was filtered the mixture. Boil the filtrate with 0.1 g decolorizing carbon. Add 0.1 g tin(II) chloride for removing the excess selenium and filter again. Concentrate the solution to 10-15 mL and keep at room temperature. Remove the crystals of alloxane (**4**) by suction filtration. The yield of the reaction was 50 % (m.p. = 168-170ºC). Alloxane becomes pink on exposure to air.

Conclusion

The reaction were described here, represent a procedure of conversion 1,3-diketones to 1,2,3-trione compounds. This method was utilized by using SeO_2-H_2O_2 as oxidizing agents and THF-H_2O as a solvent system. The temperature of reaction must hold under 50ºC for giving the best yields. This procedure shows the better results in comparison with the other methods for synthesis compounds **2**, **4** and **6**. The reactions should do under efficient safety methods.

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