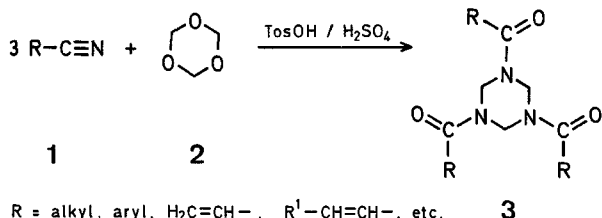


Triazines from Formaldehyde and Nitriles

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The acid-catalyzed conversion of nitriles **1** to perhydro-*s*-triazines **3** has been previously reported^{1,2,3,4}.



R = alkyl, aryl, H₂C=CH-, R¹-CH=CH-, etc.

Normally, acrylonitrile (**1**, R = H₂C=CH-) is reacted with trioxane (**2**) in benzene solvent in the presence of acetic anhydride with sulfuric acid as catalyst. The reaction goes through an induction period followed by a sometimes uncontrollable exotherm. This limits general use of the reaction.

Table. Preparation of Hexahydro-1,3,5-triacyl-*s*-triazines (**3**)

R	Yield (%)	Lit. yield (%) ^a	m.p. ^b	Lit. m.p.	Empirical formula ^c
a CH ₃	61	66 ³	95–97°	96–98° ³	C ₉ H ₁₅ N ₃ O ₃ (213.2)
b C ₆ H ₅	81	38 ³ , 95 ²	220–223°	220–222° ³	C ₂₄ H ₂₁ N ₃ O ₃ (399.4)
c H ₂ C=CH-	68	40 ³ , 89 ²	– ^c		C ₁₂ H ₁₅ N ₃ O ₃ ^d (249.3)

^a Ref. 2 reports tetrachloromethane as solvent, Ref. 3, benzene.

^b Uncorrected.

^c Compounds **3a** and **3b** gave satisfactory elemental analyses: (C ± 0.56%, H ± 0.14%, N ± 0.2%).

^d Compound **3c** gave satisfactory nitrogen analysis (N – 0.05%).

^e Compound **3c** polymerizes before melting.

We have found that a well controlled reaction can be conducted in the presence of commercial *p*-toluenesulfonic acid containing small quantities of sulfuric acid. Under these conditions the reaction shows no induction time and the exotherm is reduced dramatically. *p*-Toluenesulfonic acid alone will not catalyze the reaction. Furthermore the quantities of sulfuric acid used when employed in the absence of *p*-toluenesulfonic acid are insufficient to catalyze the reaction.

Commercial *p*-toluenesulfonic acid contains water (2 to 2.5%) and sulfuric acid (1.8 to 2.5%). The yield of triazine (65 to 68%) is independent of water content up to 4%. Above 4% the yield falls off. The yield is independent of sulfuric acid concentration in the range 1.8 to 3.5% (sulfuric acid in *p*-toluenesulfonic acid). The yield is also independent of acetic anhydride concentration.

Sulfuric and *p*-toluenesulfonic acid are playing different roles. Trioxane is probably converted to formaldehyde by *p*-toluenesulfonic acid while sulfuric acid protonates the formaldehyde. This rare catalytic combination is noteworthy because *p*-toluenesulfonic acid would be expected to protonate the formaldehyde and catalyze the reaction. A typical procedure is described below.

Preparation of 1,3,5-Triacryloylperhydro-*s*-triazine (**3**, R = H₂C=CH-):

Water (1.8 ml) was azeotroped from *p*-toluenesulfonic acid (17.2 g; Reagent grade MCB) in benzene (100 ml). Gravimetric analysis of the *p*-toluenesulfonic acid indicated nil sulfuric acid content. The solution was cooled to room temperature and acrylonitrile (179 g; 3.5 mol) followed by 100% sulfuric acid (0.3 g) was added. The solution was brought to reflux and a solution of trioxane (101.4 g, 1.12 mol) benzene (200 ml), and acetic anhydride (27.4 g, 0.26 mol) was added over a one hour period. The solution was refluxed an additional hour, cooled, and filtered. The white precipitate was washed with benzene to give the product; yield: 157.0 g (57%). The infrared spectrum was identical to that previously reported⁵. The nuclear magnetic resonance spectrum exhibited vinyl protons and a singlet methylene in a ratio of 1.7:1. Purity was determined by bromination⁶ of the three vinyl groups (98.8% of theory).

In a similar run (water was not removed) using commercial *p*-toluenesulfonic acid (1.57% H₂SO₄ by gravimetric analysis and 2.2% H₂O by Karl Fischer analysis) gave a 68% yield of the *s*-triazine.

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