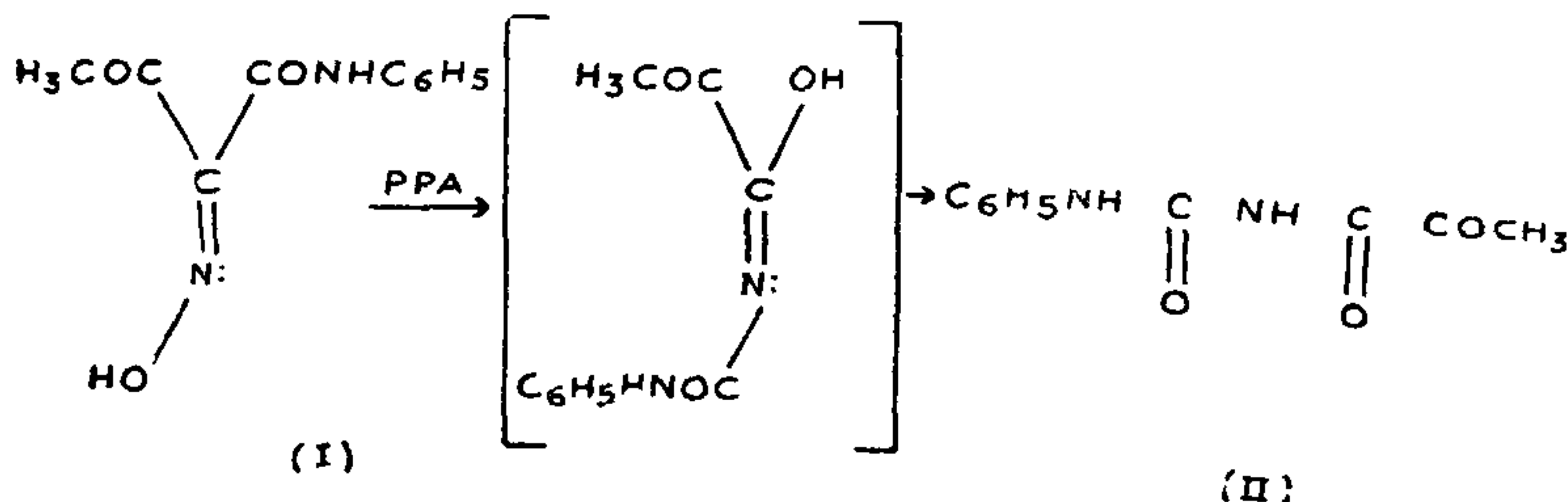


REARRANGEMENT OF ISONITROSOACETO- ACETANILIDE USING POLYPHOSPHORIC ACID TO SUBSTITUTED UREA*

POLYPHOSPHORIC acid (PPA) is a very effective reagent for cyclization-dehydration reactions¹. The cyclization of malon-monoarylamides to 2,4-dihydroxyquinolines was described by Patel and Mehta^{2,3}. The rearrangement of 3,5-dimethyl-2-cyclohexene-1-oxime to cyclic amide with PPA has been reported by Horning⁴⁻⁶.



It appeared of mechanistic interest to study the action of PPA on isonitrosoacetoacetanilide (I). In principle the reaction could give isatin or 4-acetyl-2-hydroxy quinazoline depending upon the *syn* or *anti* structures of the oxime.

It has, however, been found that treatment of (I) with PPA at temperatures ranging from 95–130° did not give either of these products and instead substituted urea (II) is formed which can be rationalized as shown above :

The structure assigned to the urea is based on analysis, hydrolysis products and chemical reaction studies. This is a general reaction as the reaction took the same course with a number of anilides of type I. The rearrangement is probably initiated by acid catalysis.

Experimental.—To the solution of PPA (81–85%) prepared from 10 g of P₂O₅ and 6 ml H₃PO₄ was added 2 g (0.01 mole) of isonitrosoacetoacetanilide and the reaction mixture heated for 1 hr at 100°. The temperature was then raised to 130° and heating continued for another 2 hr. The reaction mixture was decomposed by pouring into cold water and the solution was made slightly alkaline. The product was filtered, washed and dried. The material on recrystallisation from benzene gave 1.5 g (75%) of a product; m.p. 220°. (Found : N, 13.6; C₁₀H₁₀N₂O₃ requires N, 13.58%).

Regional Research Lab.,
Jorhat-6, Assam,
December 21, 1973.

PYARE PARIMOO.

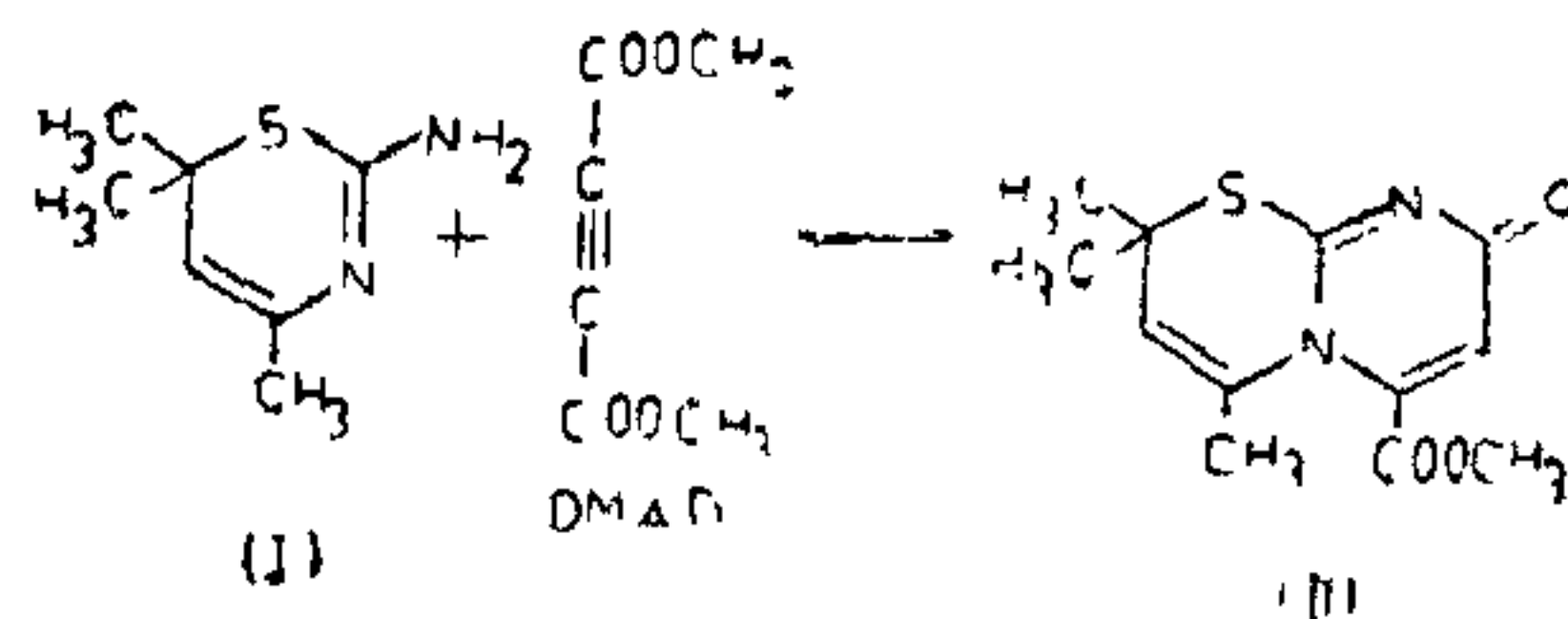
* This work was carried out by the author at Chemistry Department, University of Baroda, India.

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REACTION OF DIMETHYL ACETYLENECARBOXYLATE WITH 2-AMINO-4, 6, 6-TRIMETHYL-1, 3-THIAZINE

DIMETHYL acetylenedicarboxylate, one of the most reactive dienophiles, has played an important role in organic synthesis¹. It undergoes a wide variety of 1,3-dipolar cycloadditions², Diel's Alder type of additions³ and also is easily attacked by several nucleophiles giving rise to a variety of products⁴. The reaction of acetylenic esters with heterocyclic compounds have been the subject of several publications in recent years.

The present communication reports the addition of dimethyl acetylenedicarboxylate (DMAD) to 2-amino-4, 6, 6-trimethyl-1,3-thiazine (I)⁶ to yield the cyclised product (II) with elimination of one molecule of methanol. The structure of the product was established on the basis of various spectral and analytical data.



DMAD was added to a stirred solution of 2-amino-4, 6, 6-trimethyl-1,3-thiazine in ether at 0° C. The reaction mixture was stirred further for 2 hours. A bright yellow coloured solid was obtained which