Reaction of Enamines. I. The Preparation of Thiocarbonyl Compounds

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The reactions of enamines[1-3] have been well investigated[4-6]. We have paid attention to the reactivities of enamines and found that thiocarbonyl compounds were obtained by the reaction between enamines and hydrogen sulfide. Thiocarbonyl compounds are usually prepared by the treatment of an acid solution of the corresponding carbonyl compounds with hydrogen sulfide. This method is, however, often likely to lead to the formation of trimers, but our new method is successful in preparing monomeric compounds in good yield.

Twenty grams of 1-morpholino-1-cyclohexene[7] was dissolved in 90 cc. of dimethylformamide and hydrogen sulfide was introduced for six hours with ice cooling. The exothermic reaction occurred and the reaction mixture became faint yellow. Yellow oil separated at once when 100 cc. of 6 N hydrochloric acid was added with stirring and ice cooling.

After adding 100 cc. of water, the oil was extracted with petroleum ether, washed several times with water, dried and distilled in vacuo under nitrogen. The pink liquid, b. p.* 77~78°C/15 mmHg, with disagreeable odour was obtained, whose color was gradually faded away on standing[8].

Yield 10.0 g. (73% theoretical).

The product gave 2, 4-dinitrophenylhydrazone, m. p. 159~160°C, which showed no m. p. depression on admixture with cyclohexanone 2, 4-dinitrophenylhydrazone.

IR spectrum of the product in carbon tetrachloride solution indicated the existence of C=S bond (medium intensity band at 1130 cm^{-1}) and the lack of C=O bond of cyclohexanone (strong intensity band at 1705 cm^{-1}).

All these facts lead us to identify this product as cyclohexanethione.

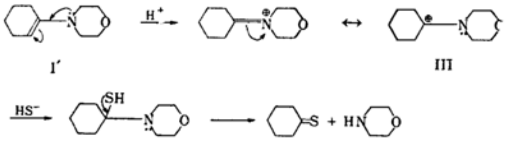
By practically the same method, cyclopentanethione was prepared in considerably good yield. From 47.4 g. of 1-morpholino-1-cyclopentene[9] in 200 cc. of dimethylformamide was obtained 23.2 g. (68% theoretical) of cyclopentanethione, b. p.** 63~65°C/8 mmHg. This gave 2, 4-dinitrophenylhydrazone, m. p. 145~146°C, which was found, by means of the mixed melting point test, to be identical with cyclopentanone 2, 4-dinitrophenylhydrazone.

IR spectrum had no absorption at 1740 cm^{-1} ($\nu_{C=O}$ of cyclopentanone).

Enamines have two mesomeric forms, enamine-form I and iminoform II.

The reaction of enamines proceeds in most cases through the attack of electrophilic reagent at β-carbon atom of imino-form II, but nucleophilic attack at α-carbon atom has also been reported[6].

It is postulated that the reaction of enamines and hydrogen sulfide occurs by the nucleophilic attack of HS$^-$ ion on the protonated enamine intermediate (III) as follows.



We continue to explore the full scope of the reaction of enamines with hydrogen sulfide. The results of the further investigation will be reported in more detail later.

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* The reported b. p.[8] 76°C/15mmHg.

** The reported b. p.[8] 86~88°C/10mmHg.