NOTES

Enamines. IV. The Reaction of 1-Morpholino-1-cyclohexene with Sulfur[1]

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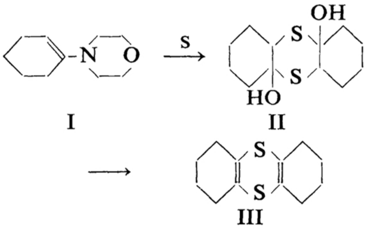
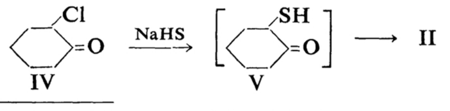
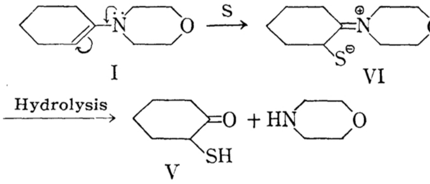
In a preceding paper of this series[2], the reaction of enamines with hydrogen sulfide was reported; in the present paper, the reaction of an enamine with elementary sulfur will be described. The heating of 1-morpholino-1-cyclohexene (I) with sulfur in the absence of a solvent gave an intractable yellow oil. By refluxing a mixture of I and sulfur in benzene, however, colorless crystals have been obtained and identified as 4a, 9a-dihydroxyperhydrothianthrene (II) by the infrared spectrum, by the elementary analysis and by the melting point test on an admixture with an authentic sample[3]. The assignment of the structure was supported by a successful conversion of II into 1, 2, 3, 4, 6, 7, 8, 9-octahydrothianthrene (III)[4] by the acid treatment.



This result may reasonably be explained by assuming the intermediate formation of 2-mercaptocyclohexanone (V), which dimerizes to a 1, 4-dithiane compound (II)[5], since Asinger et al.[3] obtained II by the reaction of 2-chlorocyclohexanone (IV) with sodium hydrogen sulfide.



It is postulated that 1-morpholino-1-cyclohexene was attacked by sulfur at the 2-position and that the resulting immonium compound (VI) was hydrolyzed to α-mercaptocyclohexanone as follows:



Such is actually the case with the Willgerodt reaction, in which Dauben et al.[6] also assumed an α-mercaptoketone as an intermediate.

II was recovered unchanged, even upon continued heating above its melting point. The OH-stretching frequency of II was observed at 3385 cm^{-1} in both Nujol and the KBr disk. Considering these facts and assuming that the 1, 4-dithiane ring is in the chair form[7], the most probable structure of II may be shown as follows (Fig. 1)*.

We expected that the 3385 cm^{-1} frequency would be shifted to the free OH region on dilution. The OH absorption of II in a carbon

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1) Presented in part at the 15th Annual Meeting of The Chemical Society of Japan, Kyoto, April, 1962. Part III of this series: Y. Takeuchi and Y. Nomura, *Sci. Pap. Coll. Gen. Educ. Univ. Tokyo*, **11**, 193 (1961).

2) Y. Nomura and Y. Takeuchi, This Bulletin, **33**, 1743 (1960); cf. C. Djerassi and B. Tursch, *J. Org. Chem.*, **27**, 1041 (1962).

3) F. Asinger, M. Thiel and H. Kaltwasser, *Ann.*, **606**, 67 (1957).

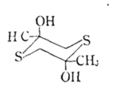
4) B. Milligan and J. M. Swan, *J. Chem. Soc.*, **1961**, 5552.

5) O. Hromatka and E. Engel, *Monatsch. Chem.*, **78**, 38 (1947); O. Hromatka and R. Haberl, ibid., **85**, 830, 1082 (1954).

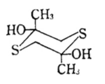
6) W. G. Dauben, R. P. Ciula and J. B. Rogan, *J. Org. Chem.*, **22**, 363 (1957).

7) Cf. R. E. Marsh, *Acta Cryst.*, **8**, 91 (1955).

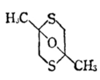
* Haberl et al.[8] isolated two isomeric forms of *trans*-2, 5-dihydroxy-2, 5-dimethyl-1, 4-dithiane (VII), the dimer of mercaptoacetone, one of which (VIIa) lost a molecule of water upon heating to give 2, 5-endoxy-2, 5-dimethyl-1, 4-dithiane (VIII), though the other VIIb was recovered unchanged.



VIIa



VIIb



VIII

They reported that the OH-strectching frequency of VIIa in Nujol or in the KBr disk was observed at 3300 cm^{-1} due to the intramolecular hydrogen bonding between OH and S, but the frequency of VIIb was observed at 3375 cm^{-1} due to the intermolecular hydrogen bond.

8) R. Haberl, F. Grass, O. Hromatka, K. Brauner and A. Preisinger, *Monatsch. Chem.*, **86**, 551 (1955).

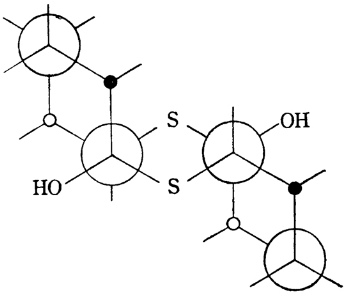


Fig. 1. Newman model of II.

tetrachloride solution, however, gradually disappeared and a strong absorption of $\nu_{C=O}$ appeared at 1710 cm^{-1}, though no absorption due to ν_{S-H} could be observed. II seems to dissociate into monomeric 2-mercaptocyclohexanone in a carbon tetrachloride solution, which has a disagreeable mercaptan-like odor.

Experimental

All melting points were uncorrected. The infrared spectra were determined on a Nihon Bunko Model Koken DS 301 spectrophotometer with a sodium chloride prism.

The Reaction of 1-Morpholino-1-cyclohexene (I) with Sulfur.—To a solution of 33.5 g. (0.2 mol.) of 1-morpholino-1-cyclohexene[9] in 100 ml. of benzene was added 4.8 g. (0.15 g. atom) of powdered stick sulfur. The mixture was heated under reflux for three hours. Refluxing was continued for two more hours after 100 ml. of 6 N hydrochloric acid had been added. The benzene layer was separated, and the aqueous layer was extracted with benzene. The combined benzene solution was washed twice with water, and the solvent was evaporated. The remaining oil was distilled in vacuo under a nitrogen atmosphere. After 1.7 g. of cyclohexanone had been distilled, 4.4 g. of a main fraction (b. p., 115~125°C/17 mmHg) was obtained; this soon solidified upon chilling. After repeated recrystallizations from 2-propanol, colorless crystals melting at 136~136.5°C (lit.[3] m. p. 135~136°C) were obtained. No depression of the melting point was observed on an admixture with authentic 4a, 9a-dihydroxy-perhydrothianthrene. Yield, 4.4 g. (25.1% based on sulfur used). IR ν_{O-H} 3385 cm^{-1} (Nujol, KBr).

Found: C, 54.92; H, 7.74; S, 24.00. Calcd. for $C_{12}H_{20}O_2S_2$: C, 55.34; H, 7.74; S, 24.63%.

A half gram of the material was heated above 160°C for two hours in an oil bath. After cooling, the almost-quantitatively recovered crystals melted at 136°C, and no depression of the melting point was caused by mixing with the initial material.

The Conversion of 4a, 9a-Dihydroxy-perhydrothianthrene (II) to 1, 2, 3, 4, 6, 7, 8, 9-Octahydrothianthrene (III).—To a solution of 0.5 g. of II in 5 ml. of 95% ethanol was added 1 ml. of concentrated hydrochloric acid, and the mixture was refluxed for three hours. After dilution with water, the acid was neutralized by sodium hydrogen carbonate. The resulting crystals were collected and recrystallized twice from 2-propanol. Yield, 0.22 g. (50% theoretical); m. p. 97~98°C (lit.[4] m. p. 97°C). IR $\nu_{C=C}$ 1610 cm^{-1} (Nujol).

Found: S, 28.58. Calcd. for $C_{12}H_{16}S_2$: S, 28.60%.

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[9] S. Hünig, E. Lücke and W. Brenninger, "Organic Syntheses", Vol. 41 (1961), p. 65.